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AGRICULTURAL RESEARCH ADMINISTRATION
BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY.

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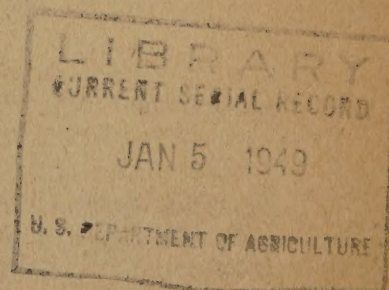
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of the
REGIONAL RESEARCH LABORATORIES
in connection with
the Eighth Annual Meetings
of the

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SOUTHERN REGIONAL RESEARCH LABORATORY

COTTON UTILIZATION INVESTIGATIONS	1
Cotton lint	1
Structure of cotton fiber.....	1
Strength of single fibers.....	1
Crystalline-amorphous ratio of cellulose.....	2
Freezing and nonfreezing water in cotton.....	2
Degradation of cotton cellulose by acidified alcohol.....	2
Carboxymethyl cotton.....	2
Phosphorylated cotton as an ion exchange material.....	2
Dye test for "mature" and "immature" cottons.....	2
Rotproofing cotton by partial acetylation.....	3
Improving weather resistance of cotton fabrics.....	4
Special finishes to improve cotton fabric qualities.....	4
Improvement of self sealing and other water-resistant fabrics..	5
Evaluation of commercial bleaching processes.....	5
The use of cotton for tire cord.....	5
Economic and technological surveys and appraisals.....	7
Cottonseed.....	8
Improving the storage properties of cottonseed.....	8
Relation of free fatty acid to germination.....	8
Basic properties of pigments.....	9
Solvent extraction.....	9
Cottonseed oil.....	10
Basic chemical and physical properties.....	10
Improvement of stability.....	10
Improvement of utility and industrial application.....	10
Cottonseed meal and protein.....	11
Properties of gland- and oil-free meal.....	11
SWEETPOTATO UTILIZATION INVESTIGATIONS	11
Simplified process for manufacture of sweetpotato starch.....	11
Commercial scale sweetpotato processing.....	11
Utilization of sweetpotato starch.....	12
Byproduct recovery and utilization.....	12
PEANUT UTILIZATION INVESTIGATIONS.....	13
Peanuts.....	13
Solvent extraction.....	13
Peanut oil.....	14
Basic chemical and physical properties.....	14
Improvement of stability.....	14
Waxlike products for industrial utilization.....	14
Peanut meal and protein.....	15
Bound water in peanut protein.....	15
Peanut protein fiber.....	15

WESTERN REGIONAL RESEARCH LABORATORY

Page

ALFALFA UTILIZATION INVESTIGATIONS.....	16
Extraction, stabilization, analysis of chloroplast pigments and other constituents.....	16
The isomers of carotene.....	16
Spectographic determination of cobalt in range grasses.....	16
Lipids and phospholipids.....	16
FRUIT UTILIZATION INVESTIGATIONS.....	17
Freezing preservation.....	17
Prefreezing treatment of pie fruits.....	17
Leaching losses during blanching of peaches.....	17
Post blanch cooling of peaches.....	17
Cold-processed gelled fruit.....	18
High-frequency heating at 3000 megacycles.....	18
Dehydration.....	18
Dehydrofreezing.....	18
Spray drying	19
Pectin.....	19
Pilot plant production of low-methoxyl pectins.....	19
Gel studies.....	19
Pectin analysis.....	20
Hydration of sodium pectate.....	20
Protein and vitamin-rich food or feed supplements.....	20
Torula yeast investigations.....	20
Enzyme preparations.....	20
Polygalacturonase.....	20
Isolation, analysis, and characterization of constituents.....	20
Phase equilibria studies.....	20
Citrus.....	21
Amino acids.....	21
Ethylene control experiments.....	21
Ascorbic acid from walnut hulls.....	21
Extraction of hulls.....	21
Crystallization of ascorbic acid.....	21
POULTRY UTILIZATION INVESTIGATIONS.....	22
Dehydrated egg studies.....	22
Storage of acidified spray-dried egg powders.....	22
Lipid deterioration.....	22
Egg enzymes.....	22
Yolk proteins.....	22
Freezing preservation.....	22
Prefreezing treatment and nitrogen packing of chickens to prevent oxidative rancidity of fat.....	22
Fibers, plastics, and adhesives from egg and feather (keratin) proteins.....	22
Cross linking in proteins.....	22
Physical-chemical properties.....	23
Isolation, analysis, and characterization of constituents.....	23
Trypsin inhibitor from egg white.....	23
Synthesis of cephalin.....	23
Fatty derivatives of phenothiazone and thionol.....	23

VEGETABLE UTILIZATION INVESTIGATIONS.....	24
Dehydration.....	24
Moisture determination of dehydrated vegetables and fruit powders.....	24
Role of moisture diffusion in drying.....	24
Static pressure drop through bin driers.....	24
Storage studies.....	24
Fluorescence as palatability index of dehydrated carrots.....	24
Dehydrofreezing.....	25
Freezing preservation.....	25
Frozen sweet corn.....	25
Volatile constituents of peas.....	25
Juice concentrates from vegetable wastes for use in the production of antibiotics and enzyme preparations.....	25
Subtilin.....	25
Proteins and protein complexes.....	26
Browning on storage.....	26
Lima bean proteins.....	26
Guar bean.....	26
Objective evaluation of reflectance color of vegetables.....	27
WHEAT UTILIZATION INVESTIGATIONS.....	27
Industrial nonfood uses of gluten.....	27
Phosphorylation of proteins with phosphoric acid.....	27
Gluten sulfate.....	27
Batch preparation of gluten sulfate.....	27
Isolation, analysis, and characterization of constituents.....	27
Lipid-protein relationship in gluten.....	27
Lipids of wheat humins.....	28
Oil of pennycress seed.....	28

<u>EASTERN REGIONAL RESEARCH LABORATORY</u>	Page
APPLE AND OTHER FRUIT UTILIZATION INVESTIGATIONS.....	29
Juice products.....	29
Processing of apple juice.....	29
Volatile flavor recovery and applications.....	29
Firming of apple slices.....	30
VEGETABLE UTILIZATION INVESTIGATIONS.....	31
Leaf proteins and other constituents.....	31
Antibiotics from onions.....	31
Amino acid analysis of vegetable leaf protein concentrates.....	32
Rutin.....	32
Agronomic studies.....	32
Analytical studies.....	33
Clinical testing.....	33
Commercial production.....	34
TOBACCO UTILIZATION INVESTIGATIONS.....	34
Recovery of nicotine from tobacco.....	34
Distillation of nicotine.....	35
Metal nicotine salts and nicotinium salts.....	35
Nicotine-DDT.....	36
MILK PRODUCTS UTILIZATION INVESTIGATIONS.....	36
Milk protein studies.....	36
Bristles from milk proteins.....	36
Structure of proteins and protein fibers.....	36
Molecular weight of lactoglobulin.....	37
Amino acid composition of alpha- and beta-casein.....	37
Carbohydrate studies.....	37
Resin and elastomer intermediates, plasticizers and solvents from lactic acid.....	37
Polylactic acid esters.....	38
Plastics, adhesives, coatings and elastomers from lactic acid.....	38
ANIMAL FATS AND OILS UTILIZATION INVESTIGATIONS.....	39
Processing studies.....	39
Stability and storage investigations.....	39
Plastics, plasticizers, coatings and other industrial chemicals..	40
POTATO UTILIZATION INVESTIGATIONS.....	40
Technology of potato starch.....	40
Storage and quality studies.....	40
Analysis of starch factory operations.....	41
Starch esters and ethers.....	42
Preparation and evaluation of allyl starch.....	42
Influence of moisture content on the keeping quality of potato starch.....	42
TANNING MATERIALS, HIDES, SKINS AND LEATHER INVESTIGATIONS.....	43
Development of new and potential tanning materials.....	43
Canaigre.....	43
Sumac.....	44
Scrub oak.....	44
Pecan shells.....	44
Development of combination vegetable-alum and other tannages.....	44
Improved curing methods for hides and skins.....	45

NORTHERN REGIONAL RESEARCH LABORATORY

Page

AGRICULTURAL RESIDUES UTILIZATION INVESTIGATIONS.....	46
Composition as affected by variety, breeding, environment, and maturity.....	46
Analysis of stalks of flint and dent type corn.....	46
Sundry new products.....	46
Noreseal--a cork substitute.....	46
Soft-grit blasting.....	46
Shotgun wads.....	47
Alcohol and other liquid fuels.....	47
Synthetic liquid fuels investigations.....	47
Butyl alcohol fermentation of xylose liquors.....	47
Motor testing of synthetic liquid fuels.....	47
Plastics, elastomers, and resins.....	48
Noreplast-R.....	48
Noreplast-L.....	48
Synthetic organic chemicals and intermediates.....	48
Hydrogenation and dehydrogenation products from furfural.....	48
Derivatives arising from opening of furan or pyran rings.....	49
Chemicals derived from fermentation.....	49
Pentonic acids.....	49
Cellulose pulps for paper and board manufacture.....	49
9-Point corrugating strawboard.....	49
Fine paper pulps from straw.....	50
Building and construction materials.....	50
Insulation and hardboard fundamental fiber studies.....	50
CORN, WHEAT, AND OTHER CEREAL CROPS UTILIZATION INVESTIGATIONS.....	51
Composition as affected by variety, breeding, environment, and maturity.....	51
Studies on development of starch granules.....	51
Oil content of corn as influenced by heredity.....	51
Composition as affected by raw material processing and storage...	51
Oil in components of the corn kernel.....	51
Alcohol and other liquid fuels.....	51
Motor tests.....	51
Fungal enzymes.....	52
Fibers, films, protective coatings, and adhesives.....	53
Fibers from zein.....	53
Plywood adhesives.....	53
Amylose triacetate fibers.....	54
Measuring orientation in fibers, films.....	54
Synthetic organic chemicals and intermediates.....	54
Formaldehyde derivatives of dextrose.....	54
Starch esters.....	54
Oxystarch.....	55
New and improved food and feed products.....	55
Microbiological vitamin synthesis.....	55
Vitamin content of cereal grains.....	55
Extraction, recovery, and properties of specific carbohydrates, oils, and proteins.....	55
Wet milling of damaged corn.....	55

Wet milling of artificially dried corn.....	56
Effect of various steeping agents on corn wet milling operations.....	56
Production of high quality glucose sirup from wheat flour.....	56
Microscopic studies of barley endosperm.....	57
Comparative studies on starches from widely different sources..	57
Pasting characteristics of starches.....	57
Properties of specific carbohydrates.....	57
Structure and other basic investigations.....	58
Degradation of amylose by α -amylase.....	58
6-a-glucosido-glucose.....	58
Chemicals derived from fermentation.....	58
Antibiotics.....	58
α -ketoglutaric acid.....	58
Production of citric acid in submerged culture.....	59
Bionic acids.....	59
Culture collection.....	59
SOYBEANS AND OTHER OILSEED CROPS UTILIZATION INVESTIGATIONS.....	59
Composition as affected by variety, breeding, environment, and maturity.....	59
Oilseed composition.....	59
Oil composition.....	59
Composition as affected by raw material processing and storage...	60
Changes in oil content of soybeans.....	60
Fibers, films, protective coatings, and adhesives.....	60
Catalytic isomerization of non-conjugated fat acids and their derivatives.....	60
Improved soybean oil paint coatings by the addition of lime....	61
Soybean protein - isolation and use in paper coatings.....	62
Shotgun shell casings.....	62
New and improved feed or food products.....	62
Flavor stability of soybean oil.....	62
Nitrogen in oil.....	63
Extraction, recovery, and properties of specific carbohydrates, oils, and proteins.....	63
Fractionation of soybean oil by liquid-liquid extraction.....	63

AGRICULTURAL CHEMICAL RESEARCH DIVISION

Page

SOUTHERN FRUITS AND FRUIT BYPRODUCTS INVESTIGATIONS.....	64
Citrus flavor essence recovery.....	64
Production of feed yeast.....	65
Histological and chemical studies.....	65
Microbiological studies.....	66
SOUTHERN VEGETABLES AND VEGETABLE BYPRODUCTS INVESTIGATIONS.....	66
Microbiological and chemical studies on cucumber pickles.....	66
BEET AND CANE SUGARS AND BYPRODUCTS CHEMICAL AND TECHNOLOGICAL INVESTIGATIONS.....	67
Aconitic acid.....	67
Sugarcane wax.....	67
Cane juice clarification.....	68
Sugar beet storage.....	68
Chemical and microbiological evaluation of beet sugar.....	68
FARM-MADE SIRUPS (SUGARCANE, SORGO, MAPLE AND MAPLE SUGAR) INVESTIGATIONS.....	68
Sorgo sirup.....	68
Candy studies.....	69
TUNG NUTS INVESTIGATIONS.....	69
Drying, milling and oil extraction of dehulled nuts.....	69

LABORATORY OF FRUIT AND VEGETABLE CHEMISTRY

Citrus.....	70
Standardization of desert grapefruit juice.....	70
Freezing preservation of citrus purees.....	70
Keeping qualities of chilled fresh citrus juice.....	70
Freezing preservation of citrus segments.....	70
Quick freezing of citrus juices.....	71
Canned tomato paste.....	71
Chemical composition of commercial tomato paste.....	71

FRUIT AND VEGETABLE PRODUCTS LABORATORY

Fruit Products.....	72
Freestone peach canning investigations.....	72
Canning investigations on apricots.....	72
Detartration studies on grape juice.....	72
Prefreezing treatments of freestone peaches.....	73
Vegetable products.....	73
Froth flotation process.....	73
Canning technology of Pacific Northwest vegetables.....	73
Freezing technology of Pacific northwest vegetables.....	73

ENZYME RESEARCH LABORATORY

Page

Stimulation of ripening by ethylene.....	75
Enzymes connected with the metabolism of citrus and the quality of fruit.....	75
Changes in starch digesting enzymes (amylases) caused by ripening.....	75
Ripening and changes in fat.....	76
Phytochemical studies.....	76

DIVISION OF BIOLOGICALLY ACTIVE COMPOUNDS

BASIC INVESTIGATIONS IN THE CHEMISTRY OF AGRICULTURAL PRODUCTS.....	77
Investigations on the biochemistry of plant disease resistance.....	77
Investigations on the mechanism of action of plant growth regulating substances.....	77

PHARMACOLOGY DIVISION

PHARMACOLOGY INVESTIGATIONS.....	79
Citrinin.....	79
Nicotine derivatives.....	79
Rutin.....	79
Ascorbyl palmitate.....	79
Cottonseed meal.....	79
Continuous saccharification process.....	80
Starch powders.....	80

MICROBIOLOGY RESEARCH DIVISION

Microbiology of dried eggs and related egg products.....	81
Occurrence of multiple salmonella types in spray dried whole egg powder.....	81
Paracolon organisms in spray-dried whole egg powder.....	81
Incidence of salmonella types in and on shell eggs.....	81
Effect of holding and scrambling on salmonella in reconstituted egg powder.....	82

NAVAL STORES RESEARCH DIVISION

Page

INVESTIGATION OF NAVAL STORES PRODUCTION, PROCESSES AND EQUIPMENT.....	83
Processing of pine gum.....	83
Studies of cup and gutter materials.....	83
INVESTIGATION OF THE COMPOSITION, COMPONENTS AND DERIVATIVES OF NAVAL STORES.....	83
Synthetic elastomers from turpentine derivatives.....	83
Chemical derivatives of the pinenes.....	84
INVESTIGATION OF THE USES OF NAVAL STORES.....	84
Purification of dehydrogenated rosin.....	84
Utilization of resin acids.....	84
Compilation of statistics.....	84

SOUTHERN REGIONAL RESEARCH LABORATORY
Walter M. Scott, Director

COTTON UTILIZATION INVESTIGATIONS

COTTON LINT

Structure of Cotton Fiber

The shape of individual cotton fibers and the dimensional changes which they undergo on wetting with water are related to the performance of many cotton products and to research on improving the serviceability of textiles for various uses.

Cross sectional dimensions of both wet and dry cotton fibers have been measured on photomicrographs of cross sections obtained by imbedding the fibers in methyl methacrylate according to a specially developed technique. Cross sectional area was measured with a planimeter and perimeter with a perimetron developed for the purpose at the Southern Laboratory. Changes due to mercerization have also been measured, showing increase in area and decrease in perimeter for every cotton variety tested.

A fiber orifice test has been derived from the yarn orifice test to provide a means of evaluating different raw cottons for use in self-sealing fabrics. The results obtained in most cases parallel those obtained with the yarn orifice test.

Three distinct methods are being investigated as indirect measures of the water swelling capacity of cotton. All three measure the most firmly held water in wet cotton. They measure, respectively, water retained by wetted fibers after (1) centrifuging, (2) hydraulic expression of the water, and (3) drying over a desiccant.

Strength of Single Fibers

The relationship of fiber strength to fiber length in a given cotton variety is being determined by means of the single fiber strength tester developed at this Laboratory. Samples of cotton are sorted into uniform length groups and fibers from each length group are tested separately. In general, the strength of individual fibers decreases with increasing length. This, however, is due to an increase in fineness with increased length, for the strength per unit area increases with length.

Measurements of the static endurance of single fibers and of cords made from the same cotton have shown the behavior of both the single fibers and the cords to be governed by the same laws. This is in agreement with similar studies made on flexure endurance.

Crystalline-Amorphous Ratio of Cellulose

The acid hydrolysis method for determining the crystalline-amorphous ratio has been investigated very carefully from the standpoint of sample preparation. Since grinding to finer particle size decreases the ratio of crystalline to amorphous material, it is necessary to control closely the grinding of analytical samples.

Freezing and Nonfreezing Water in Cotton

The relative amounts of freezing and nonfreezing water in cotton fibers of different types have been determined calorimetrically, and the results have been interpreted on the basis of the generally accepted structure of the cotton cellulose. Estimations of the crystalline-amorphous ratio made from these data agree fairly well with those determined by acid hydrolysis of the fiber.

Degradation of Cotton Cellulose by Acidified Alcohol

The degradative action of methyl alcoholic acid solutions on cotton cellulose has been further followed using a specially developed analytical method for the determination of glucosidic methoxyl. The alcoholysis rates at various temperatures are now being determined. The new method is being applied to other fundamental investigations of cellulose.

Carboxymethyl Cotton

If cotton is made to react with monochloroacetic acid in the presence of mercerizing caustic, carboxymethyl group may be introduced into the cellulose molecule with a resulting increase in swellability by water.

Optimum conditions have been established for the addition of one such group per 20-25 glucose residues. This amount of substitution gives a more quickly swellable yarn without greatly affecting appearance, hand, or strength as compared with a corresponding mercerized yarn. When these treated yarns were woven into cloth, however, there was no improvement in the impermeability of the cloth to water. A number of metal salts of the carboxymethylated yarns and cloth have been prepared. The copper, silver, and mercury salts have been found to be comparable in their resistance to microorganisms to cotton impregnated with copper naphthanate.

Phosphorylated Cotton as an Ion Exchange Material

Phosphorylated cotton cellulose, having one phosphate group per 1-2 glucose residues, has been tested as a cation exchanger. The exchange capacity is high, averaging more than 1,000 milli-equivalents per kilogram, which compares favorably with commercial ion exchange resins. The sample tested failed after 4 months of use, apparently owing to age.

Dye Test for "Mature" and "Immature" Cottons

Work at the Southern Laboratory in cooperation with a large

southern mill which had encountered difficulties in the manufacturing and dyeing behavior of a certain type of cotton led to the development of a comparatively simple method for determining certain important qualities of cotton. It was found that the trouble experienced was caused by the presence of an unusually large proportion of flat-shaped, thin-walled undeveloped fibers commonly referred to as "immature" cotton. The method distinguishes between the "immature" and the full-bodied normal cotton by utilizing the differential dyeing characteristics of these two types of fibers. For example, a sample of the cotton is taken from the bale and dyed in a bath containing a mixture of a specially selected red and green dyes. On removal from the dyebath certain fibers have dyed green while others have dyed red. Microscopic examination shows that the green-dyed fibers are the "immature" fibers while the red-dyed fibers are fully matured.

The application of this differential dyeing technique is being studied further. It promises to be of considerable value to those interested in studying the development of seed cottons of particular varieties and strains from their early stages of growth. Cotton manufacturers are interested in the possibility of using the technique to weed out bales of "immature" cotton which might be difficult to process, one firm advising that a shipment of several bales was rejected on the basis of this test.

Rotproofing Cotton by Partial Acetylation

A highly rot-resistant cotton prepared through the chemical modification of cotton yarn and cloth by a process of partial acetylation has been described in previous reports. This relatively new product has advantages over ordinary rotproofed goods in that it is not discolored, odorous, sticky, nor toxic.

Since partially acetylated cotton is not yet being manufactured for the market, it is being produced at the Southern Laboratory, in both yarn and cloth form, on a pilot-plant scale with commercial-type machinery for service trials for various purposes. Yarn, which is being acetylated in the package dyeing machine in amounts up to 6-10 pounds per run, is proving of particular interest for fishing gear. The main interest at present is in use of the cloth, which is being acetylated successfully at full width on a dye jig in lengths up to 75 yards, is as a base fabric in "varnishing" for electrical insulation, and in lamination with plastics. Important properties which partially acetylated fabric possesses for such uses are electrical resistance and heat resistance. The latter property may be of value in curing as well as during service. Although partially acetylated cotton is considered heat-resistant, it has plastic properties at relatively high temperatures, and these are being studied as of possible advantage in certain uses.

The modified cotton has proved to be the best material yet found for bags subject to rotting in domestic water-softening systems. Samples are also on trial for use in protecting hams in overseas shipments; for covering cheeses; and for use in shoe lining, seedbed covers, and sewing thread for outdoor exposure.

Improving Weather Resistance of Cotton Fabrics

Research on weathering of cotton fabrics is now almost entirely concerned with determining, as accurately as possible, the part played by the individual destructive forces involved in weathering, as a guide to development of improved finishing treatments.

A special exposure cabinet has been constructed in which fabric samples may be subjected under controlled conditions to the action of different wave lengths found in solar radiation. With use of this normal incidence exposure cabinet, data have been collected through the year on ambient air temperature and humidities inside the cabinet; temperatures, humidities, and rainfall outside the cabinet; and on the radiant energy incident upon the samples. Data have also been collected on the fluidity and breaking strength changes in identical fabric samples exposed to the energies in each of five different spectral regions as well as to total radiation.

As a preliminary to the investigation employing this special apparatus, data had been obtained with use of a carbon arc lamp as a source of radiation and Corning glass filters as a means of obtaining certain selected spectral regions of incident energy. The results tend to substantiate the theory that certain wave length regions in the spectrum may interact in such a manner as to reduce the net degrading effect on cotton cellulose of the total incident energy. Thus clear glass has a slightly greater protective effect when used to screen a sample of cotton fabric from carbon arc radiation than does blue glass even though the latter has a lower transmission throughout the spectrum. Observations were made of the bleaching and yellowing action of radiant energy of various spectral distributions under several conditions and showed no direct relation between this effect and degradation.

Weathering breakdown of unprotected cotton cloth has been studied in a series of exposure tests conducted over the past 5 years. By combining data secured from replicate samples exposed for equal periods of the time but at different seasons of the year, year-round weathering patterns have been obtained for representative cotton constructions that serve as dependable standards of reference in the evaluation of protective treatments. Changes in breaking strength and cuprammonium fluidity have been employed as the chief criteria of degradation. Since it has been demonstrated that biological attack of cotton lowers the breaking strength without materially influencing fluidity in the surviving material, while the action of sunlight apparently causes concurrent strength and fluidity changes, a study of the strength-fluidity relationships affords considerable information about the different types of degradation that occur in seasonally exposed samples.

Special Finishes to Improve Cotton Fabric Qualities

The attractive fabrics prepared in semicommercial-scale finishing of low-grade osnaburg and bag sheeting by combining mercerization with the application of a durable-type modified cellulose finishing agent have been described in previous reports. While the finishing agent employed, an alkali-soluble hydroxy ethyl ether of cellulose, is fairly effective

in preserving the hand and appearance of cotton goods in actual service, it contributes nothing to crease resistance, a property in which cotton is deficient. The well known urea formaldehyde and melamine resins are being reexamined to obtain accurate data on the maximum crease resistance that can be imparted without adverse effect on the strength and tear resistance of the fabrics. The results to date support the commonly accepted view that new resins or improved chemical processes will have to be developed before satisfactory crease resistance can be secured.

Improvement of Self Sealing and Other Water-Resistant Fabrics

The work on fabrics that resist the passage of water through swelling of the constituent cotton fibers has progressed from unlined fire-hose to wind- and rain-resistant army oxford fabrics. A project to improve the water resistance of this type of cotton fabric has been undertaken in cooperation with the Quartermaster Corps.

It has been demonstrated that cottons differ in their ability to close the minute spaces that exist in tightly woven fabrics. An oxford fabric of greater water resistance has been obtained by using "immature" or thin-walled cottons, rather than comparative cottons which are nearer normal and of better quality according to usual standards. It has been shown also that the water resistance of other cotton fabrics can be increased by adding a swellable material to the yarn prior to weaving.

These principles will be studied further and fabrics of different constructions will be manufactured and service-tested as outer clothing, tarpaulins, tents, farm fabrics, etc.

Evaluation of Commercial Bleaching Processes

The evaluation of fabric samples taken at the important steps in eleven commercial bleaching processes has been completed and the data have been put into form for publication as a Department bulletin. The findings indicated that some changes could be made in common bleachery practice which should result in lower production cost and better quality output. With this cross section of performance as a start, it is planned to study the newer continuous methods more intensively and to extend the work to types of processes not yet sampled.

Current research on kier boils and bleaches will be extended to include a survey of the use of detergents to determine their actual value in kier boiling. In connection with the broader aspects of the bleaching project, there has been some preliminary study of open-width scouring with special reference to army requirements.

The Use of Cotton for Tire Cord

The coordinated program of research for developing improved types of cord has continued to be a major activity at the Southern Laboratory. Since the end of the War objectives have been altered somewhat, primary consideration being given to the service requirements of cord in tires for civilian use.

Service tests begun in April 1946 are still under way on 9.00-20, S6 (67% GRS and 33% natural rubber), 10-ply cotton cord tires made with (1) Goodyear regular production cotton cord, and (2) Wilds cotton cord produced according to the dual-stretching process developed at the Southern Laboratory. A similar set of rayon cord tires is being run along with the cotton tires to obtain comparative data on growth, tread-wear, and operating temperatures. As of January 1, 1947, no failures had yet occurred which could be ascribed to the tire cord. Four tires had to be discarded because of cuts caused by spikes and glass.

A series of wheel-test trials has been completed by the National Bureau of Standards, with results similar to those obtained previously in Goodyear's Laboratory. The regular commercial cotton-cord tires gave the lowest mileage, the rayon-cord tires the greatest, while the two groups of Wilds cotton-cord tires gave intermediate mileages. An attempt will be made to correlate these results with those obtained on the road-tested tires.

A ply-building machine has been constructed, the use of which will facilitate the manufacture of tires for small-scale wheel and road tests. With this machine, plies can be made from a single end of cord, the quantity required being only slightly in excess of the actual poundage of fabric in the finished tire. The plies so made are cut to the proper bias angle and shipped to a tire plant where they are made up into bands and thence directly into tires, by-passing the dipping and calendering operations completely.

Determination of hysteresis, elastic modulus, and elongation growth at various moisture contents and temperatures on seven tire cords (two rayon, four cotton, and one nylon) has brought out a number of significant facts. In general, moisture content over the ordinary ranges has a much greater effect on the elastic properties than does temperature up to 145° C. Hysteresis increases, elastic modulus decreases (except for the cotton cords at less than 5% moisture) and elongation growth rate increases with increasing moisture contents for all cords. The next phase of the work projected in this field is to set up an electronic apparatus for routine determinations at speeds of approximately 19 cycles per second--10 times the present rate.

Research has been continued on the influence of cord construction on cord properties, using 17/4/3 construction with three different staple lengths of cotton (1", 1-3/32", and 1-3/8") as the basic cords. It was found that the amount of twist in the single yarns is a relatively unimportant factor in regard to strength and flex-life, and that a slightly higher ply-twist than is customarily used commercially gives greatest flex-life. To investigate the effect of varying the number of ends in the ply and cord, using the same twist multiplier in the ply which gave highest flex-life in the "basic" cord, 1-3/32" Stoneville 2B cotton was made up into 0.032 and 0.026 gauge cords of five different constructions, 5/2, 4/2, 5/3, 4/3, and 3/3. The strength of all of these constructions was practically the same for each gauge, but the flex-fatigue life, as measured on two types of flex machines, was decidedly greater for the 3-cable construction.

To establish more general relationships between cord construction and cord properties, a 1-3/8" Wilds cotton is being studied over a wider range of constructions, from 2/2 to 5/5.

Close contact has been maintained with tire and tire cord manufacturers for the purpose of receiving accurate, up-to-date economic and technical data and of exchanging experimental data concerning the use of cotton and competing fibers in tire cord.

Economic and Technological Surveys and Appraisals

Economic research has been continued in cooperation with other agencies in a program sponsored by the Cotton Subcommittee of the House Committee on Agriculture to study the postwar agricultural and economic problems of the cotton belt.

A survey of rayon as a competitor of cotton (Project V) was completed and a report is being processed. According to the report, domestic production of rayon more than doubled between 1939 and 1945, reaching 782 million pounds in the latter year. Expansion to around 1.1 billion pounds annually (the equivalent of about 2.6 million bales of cotton) is expected by 1950. Rayon prices, stable during World War II, unlike the prices of cotton and wool, were increased slightly in November 1946. It was concluded that while rayon prices will continue to be quite stable, reductions of not more than a few cents per pound are possible in the next few years.

Also as part of the House-sponsored cooperative economic research program, several short-time surveys have been made of the competitive position of cotton in major end-use markets (Project IV).

One of these surveys was of the use of cotton and competing materials in tire cord. It was found that almost all truck and bus tires and some of the heavier passenger car tires are now made of rayon cord. While in very large truck and bus tires, rayon cords give performance superior to that of the present types of commercial cotton cords, the latter are entirely satisfactory in passenger car tires. At the current prices of rayon and cotton fabrics, however, the manufacture of all types of tires with rayon is cheaper. It is estimated that in 1950, assuming highly prosperous conditions, only a maximum of about 40 million pounds of cotton cord would be used as compared to about 200 millions pounds of rayon cord. With moderately prosperous conditions, only about 25 million pounds of cotton cord would probably be used as compared to an estimated 150 million pounds of rayon. These predictions assume a price of 25 cents per pound for Middling 15/16-inch cotton. At 12 cents per pound, cotton would probably hold all of its market in passenger tires and regain some of the ground lost to rayon in the truck-tire market.

A survey of cotton's competitive position in bags showed that consumption of cotton in this use climbed to 820,000 bales in 1943 owing largely to increase in wartime packaging requirements accompanied by curtailment of imports of burlap from India. With burlap once more available and the use of paper increasing, this figure dropped to 440,000 bales in 1946. While cotton will face continued competition

from burlap and growing competition from paper in use for bags, in 1950 bags are expected to be the largest single end use of cotton, with an estimated consumption of 575,000 bales under highly prosperous conditions, and 536,000 bales under conditions of moderate prosperity. These estimates are on the basis of a price of 25 cents per pound for cotton.

A study of farm incomes in the Southern Laboratory's region showed that agriculture's contribution to total income from all sources in the region declined from 27% in 1929 to 22% in 1939 and to 21% in 1944. Probably the most significant trend indicated by the survey was the growing importance of livestock and diversified farming in the agricultural economy of the South. Since 1941 livestock and livestock products have been a more important source of income than cotton, still the largest farm crop.

Short-time surveys have also been made on such subjects as the following: relationship of raw material, labor, and overhead costs in the dyeing and finishing industry; possible uses of surplus nylon rope; and the factors involved in the possibility of establishing a cordage and twine plant in the Gulf Southwest area. A preliminary survey also was made to determine general fields where marketing research on cotton is particularly needed.

COTTONSEED

Improving the Storage Properties of Cottonseed

In continued investigations of the enzyme systems of cottonseed and the nature of their activation and inhibition, the biochemical activity of over 200 chemicals has been measured by a recently developed technique. In the technique the chemical to be tested is added to 300 grams of seed placed in a thermos bottle, the effect on heating is followed by measurements of temperature of the sample, and the inhibition of lipolysis is followed by measurements of the free fatty acid content of the sample after 6 days in storage. Among the more active compounds evaluated by this laboratory test are the following: ethylene chlorohydrin, 1,3-Dimethyl-4,6-bis(chloromethyl) benzene, phenol, and propylene glycol dipropionate. Most of the tests were made initially on flaxseed because it is easily handled and responds in a quantitative and reproducible manner. The enhancement of biochemical activity by use of surface active agents is also being investigated.

Three mill-scale experiments on the 1946 cottonseed and flaxseed (South Texas) crops are in progress in order to test the effectiveness of ethylene chlorohydrin by different methods of application under different conditions. Mill-scale experiments during the processing of the 1947 crop will be made using other compounds found promising by laboratory tests.

Relation of Free Fatty Acid to Germination

Some data have been obtained on the relationship of free fatty acid to germination in individual cottonseeds by a chemical analysis of one

part of a kernel employing micro techniques, and by germination of the other part on agar. The results showed that most seeds with a free fatty acid content (based on weight of seed) of less than 1.8% will germinate. Seeds with a free fatty acid content of 4.8% or more did not germinate. Unfortunately, among 299 individual seeds tested, none were found that had a free fatty acid content between 1.8 and 4.8%. This "blank space" may be due to the "autocatalytic" nature of the formation of free fatty acids in cottonseed. Attempts to fill this gap will be made.

Basic Properties of Pigments

New data continue to be obtained on the nature and occurrence of cottonseed pigments. The gossypol and gossypurpurin content of a series of samples of pigment glands was determined and compared with the content of these two pigments found in the corresponding seed. The results indicated that all the gossypol and gossypurpurin are segregated in the glands and constitute essentially all the pigments of the glands.

The pale yellow pigments occurring outside the glands were removed by extracting dry seed with light petroleum naphtha. Although similar to gossypol in color, this pigment fraction of cottonseed is chemically quite different; it does not react with antimony trichloride, is relatively stable, is nonpolar and nonacidic.

Solvent Extraction

Chemical engineering research on solvent extraction of cottonseed has had three main objectives: the further development of a solvent process for gland separation used successfully on a laboratory scale; the design and development of equipment to carry out batch solvent processes; and the production in sufficient quantities of cottonseed materials needed for various research purposes.

Gland separation process. Research on the gland separation process by which cottonseed meats are fractionated into pigment glands, oil, and oil- and gland-free meal has been primarily concerned with the production of the gland and meal fractions for investigations of a fundamental nature. Using pre-pilot-plant-scale equipment, 51 pounds of highly purified pigment glands and corresponding amounts of meal and oil were obtained in processing approximately 2900 pounds of cottonseed meats. The gland and meal fractions of high purity, available in test quantities for the first time, are making possible the determination of many fundamental properties -- information long needed by the cottonseed industry.

Preliminary considerations are also being given to the development of possible uses for pigment glands, since this product would be available in quantity should a gland separation process be introduced commercially.

The oil-solvent fraction was concentrated, steam-stripped, and vacuum-dried for removal of solvent. Several samples of the oil, refined and bleached using standard procedures for hydraulic-pressed

products, were found to be prime with respect to color.

As better techniques and improved equipment are developed, larger lots of cottonseed meats are being processed in the pilot plant. Experiments now planned include the use of a centrifuge for continuous separation of the glands. The gland separation process is still under development with the scale of the pilot plant research being expanded to determine the commercial feasibility of the principle of processing.

Batch extraction process. Single cell extractors of 120 pound capacity and necessary auxiliaries were built and operated for the production of solvent extracted cottonseed oil and meal. Approximately 830 pounds of flakes were extracted with hexane or diethyl ether as the solvent. An oil extraction efficiency of 99% or better was attained with both flakes and meal. With specially designed evaporator and stripping columns a solvent-free oil was obtained from the miscella. The meal was first air dried and then vacuum dried for complete removal of the solvent.

COTTONSEED OIL

Basic Chemical and Physical Properties

Comparison of the pigmentation of hydraulic-press oils with that of screw-press oils shows that the principal factor responsible for the more highly colored oils obtained by the screw-press method is the lower moisture content of the seed during cooking. The conversion products of gossypol (pigments) found in the crude, screw-pressed oils are entirely different from those found in the crude, hydraulic-pressed oils, and are less effectively removed by the standard refining and bleaching procedures. Consequently, to obtain screw-pressed oils of color quality comparable to that of hydraulic-pressed oils, either the cooking conditions in the screw-press method or the refining procedures require alteration.

Improvement of Stability

In an investigation of hydrogenated vegetable oils no direct linear correlation was found between keeping quality and fatty acid composition. The reciprocal of the keeping quality was found, however, to be linearly related to the linolein content of either cottonseed or peanut oil.

Improvement of Utility and Industrial Application

A series of purified mono-, di-, and triglycerides were prepared from cottonseed oil, varying amounts added to pure peanut oil, and the interfacial tension was measured against water at 70° C. The results indicate that the surface activity of diglycerides is less than 1/100th that of monoglycerides, on a weight basis. The addition of 1% monoglyceride to the pure oil will decrease the interfacial tension at oil-water interface by 50%, while 6% concentration of monoglyceride in the oil phase will lower the surface tension approximately to zero.

COTTONSEED MEAL AND PROTEIN

Properties of Gland- and Oil-free Meal

The gland- and oil-free meal produced in the pre-pilot-plant-scale research has varied from almost colorless to a pale yellow, has contained from zero to 0.04% gossypol, a trace of a yellow decomposition product of gossypurpurin, and has had an oil content averaging about 0.5%.

Several hundred pounds of this high-purity meal have been furnished Federal, industrial, and university laboratories for nutritional and pharmacological investigations involving rats, mice, guinea pigs, rabbits, chicks, and hens. These investigations are still under way but on the basis of observations to date some conclusions can be drawn. All of the objectionable properties of raw cottonseed meals are concentrated in the pigment glands and are due to some constituent of the glands other than gossypol. The gland-free cottonseed flour has been shown to be superior to hydraulic-pressed meal and soybean meal with respect to effect on growth and reproduction of experimental animals.

SWEETPOTATO UTILIZATION INVESTIGATIONS

Simplified Process for Manufacture of Sweetpotato Starch

The yield and quantity of product obtained in pilot-plant scale research encourages the prospect of completing the development of a simplified process for the manufacture of starch from sweetpotatoes. Such a process will increase the feasibility of small plant units of low cost and overhead.

In 17 pilot-plant runs approximately 12,000 pounds of sweetpotatoes, mostly of the L-5 variety, were ground and processed. Effort was concentrated on determining the efficiency with which crude starch milk from the regular grinding and screening system can be freed from solubles and nonstarch solids by means of several combinations of batch- or continuous-type centrifugals and fine screens. The sodium hypochlorite bleaching procedure was varied in a number of runs in order to ascertain the effect of variation on viscosity characteristics of the starch obtained in these simplified processes.

Leading manufacturers are being consulted with respect to available equipment suitable for simplified starch processing, giving particular attention to continuous solid-bowl centrifugals for use in lieu of batch-type solid basket machines, equipment for fine screening in refining starch milk, and starch-drying equipment.

Commercial Scale Sweetpotato Processing

The new sweetpotato starch factory of the United States Sugar Corporation resumed operations for the current season on December 3, 1946. In the interim since termination of last season's operations at the end of March 1946, continued technical advice and assistance were

rendered in respect to certain needed improvements in equipment, process, and operating procedure. A number of further changes and adjustments in processing units are considered desirable; but for the most part the equipment and the processes are satisfactory and capable of turning out the maximum estimated production of about 120 tons of starch a day.

Production is still on a reduced capacity chiefly because of the limited quantity of sweetpotatoes available. Yields and quality of the raw material, however, are far better than in the preceding season. Some difficulties are still encountered in carrying field production to the volume necessary to sustain the large factory at full capacity, without excessive cost for raw material. Problems not forecast by the results of the previous experimental plantings have developed. It is likely that, with termination of the present processing season, further curtailment, or even suspension of the factory operations may be necessary until crop production problems have been solved by further development work.

Utilization of Sweetpotato Starch

With the cooperation of a cotton textile mill warp sizing tests conducted on a series of sweetpotato starches obtained primarily in pilot-plant research showed that these starches gave superior performance, required less softener, and consequently gave a less costly size mixture.

A number of samples of sweetpotato starch of different types have been furnished to industrial and research organizations for experimental purposes.

Byproduct Recovery and Utilization

For every 100 tons of sweetpotatoes ground, the overflow fruit water from settling or centrifuging in the sweetpotato starch manufacturing process as carried out so far, contains an average of about 3500 pounds of sugars and about 2300 pounds of protein which are now wasted to the sewer. Pilot-plant-scale experiments have indicated the feasibility of economically recovering from the waste water around 1-1/2 tons of protein concentrate and of producing from the sugars nearly 3/4 of a ton of feed yeast for every 100 tons of sweetpotatoes processed.

A complete pilot plant, with all accessories and controls for continuous and practically automatic coagulation of the natural protein and the continuous propagation of *Torula* yeast has been designed and assembled at the Southern Laboratory. The equipment permits production of yeast alone or combined recovery of yeast and protein. After preliminary trial in New Orleans, the equipment was moved to Orlando, Florida, and erected in a building provided by the Dr. P. Phillips Company for trial with citrus pulp and press juice. The engineering and operating problems are essentially the same for either sweetpotato fruit water or citrus press juice.

The trial runs indicated the need for a number of mechanical adjustments. With elimination of some of these deficiencies (in particular, the problem of excessive foaming), and with improved accessory equipment, it will be possible to determine the optimum conditions of nutrient

amendment, rates of feed of media, and aeration.

With large-scale pilot plant equipment available for both feed yeast production and recovery of feed protein from sweetpotato starch fruit water, sufficient quantities of these byproducts can be obtained to permit evaluation of their quality and value as feed supplements. The feasibility of sweetpotato starch manufacture will be enhanced through increased byproduct credit.

PEANUT UTILIZATION INVESTIGATIONS

PEANUTS

Solvent Extraction

Chemical engineering research on solvent extraction of peanuts has been principally concerned with the design and development of equipment for solvent extraction by continuous processes and the production of solvent-extracted peanut materials in batch operations for various research purposes. From 17,000 pounds of whole peanuts approximately 11,400 pounds of whole meats (with 700 pounds of fines) have been prepared for solvent extraction

Batch extraction process. Ten batches of peanut meats totaling 1200 pounds were cracked, flaked, and solvent extracted in a batch extractor to produce 620 pounds of meal containing less than 1% of oil for use in research on protein fibers and protein adhesives. Oil and solvent were recovered from the miscellas.

Continuous extraction processes. The continuous solvent extraction equipment, constructed for use with either peanut or cottonseed flakes, is of the screw-conveyor type. It is designed to extract 150 pounds of flaked meats per hour, producing a miscella of 10 to 20% oil by weight. An oil and solvent recovery unit, which may be operated simultaneously with the extraction unit, was designed for a capacity of 150 lbs. per hour of peanut oil from a miscella containing 10% oil by weight. Commercial hexane (Skellysolve B) was selected as the solvent because of its low boiling point, general suitability for extraction purposes, availability, and low cost.

Serious handling problems are encountered due mainly to the fragility of the peanut flakes which break up during extraction operations with production of a considerable quantity of fines. Although none of the experimental runs so far made have been wholly satisfactory, the tests have yielded valuable engineering information. Changes in equipment and in conditions of operation are being made which should render the process suitable for consideration in commercial scale processing.

PEANUT OIL

Basic Chemical and Physical Properties

For predicting the behavior of fat-solvent systems in practical fractional crystallization operations, a series of fat-solvent systems containing more than one fatty component was examined. Investigations of the solid and liquid phases in the system stearic acid - oleic acid - commercial hexane in the temperature range 0° to -40°C . and of the system oleic acid - stearic acid - acetone, at 0° , -10 , and -20°C ., showed that oleic acid and stearic acids are both more soluble in acetone than in commercial hexane at any given temperature; but that the presence of oleic acid increases the solubility of stearic acid more in the hexane than in the acetone. Appreciably greater quantities of oleic acid were removed from the liquid phase at higher temperatures in acetone than in hexane.

From the family of curves obtained with phase diagrams constructed at each isotherm, it is possible to predict the degree of separation obtainable in any mixture of oleic and stearic acids with either acetone or hexane used as solvent. Furthermore, the choice between these solvents, depending upon results desired, will be indicated.

Improvement of Stability

Work on improving the keeping quality of peanut oil has included research on the stabilizing action of norconidendrin; on the effect of adsorbents; and on the correlation of keeping quality with fatty acid composition.

The tests with norconidendrin showed that this compound, either alone or in combination with acid-type synergists, has good antioxidant activity in edible-grade peanut oil and in one freed from naturally occurring antioxidants. The treatment with adsorbents showed that application of aluminosilicate to a hydrogenated peanut oil having an iodine number of 60 resulted in an improvement in keeping time of 21% and of 74% when the same adsorbent was activated by redrying. The results obtained to date in an investigation of the reaction between the component unsaturated fatty oils of peanut oil and maleic anhydride support the explanation generally proposed for the oxidative deterioration of fats.

Waxlike Products for Industrial Utilization

Research has continued on the preparation of waxlike esters containing amino or amido groups with the objective of obtaining products satisfactory as replacements for natural vegetable waxes, in particular, in the manufacture of carbon paper inks. The reaction product of 2 mole equivalents of stearic acid and 1 mole equivalent of 2-amino-1-butanol had dispersing properties equal to those of some of the poorer vegetable waxes, but did not have adequate oil retention properties. The purified product was superior to the crude product, free fatty acid content being reduced by purification. Compounds prepared by the reaction of stearic acid with monoethanolamine and with 2-methyl-2-amino-1-propanol were inferior in dispersing power to the 2-amino-1-butanol compound, but had better oil retention properties.

In view of the present uses of long-chain aliphatic amines as plasticizers, flotation agents, and detergents, attempts are being made to prepare a number of N-phenyl amines, such as the N-phenyl dodecyl and octadecyl amines, by reduction of the corresponding anilides.

PEANUT MEAL AND PROTEIN

Bound Water in Peanut Protein

Research on the basic physical and chemical properties of peanut protein has included an investigation of the effect of heating on the bound to free water relation by means of the calorimetric "heat of fusion" method. Samples of protein were held for varying lengths of time at temperatures ranging from 25° to 77°C. The results indicate that heating to any temperature above 40°C. in the range studied increases the amount of bound water from about 10% to about 18%, this amount decreasing, however, with the denaturation of the protein that occurs at the higher temperatures.

Peanut Protein Fiber

Sarelon is the name given to peanut protein fiber produced at the Southern Laboratory by a "wet" process similar to that employed in the viscose rayon industry. Sarelon is cream colored with a soft hand intermediate between that of silk and wool and has a warm feel upon contact with the skin, absorbing moisture in a manner similar to wool. It does not shrink appreciably in hot water and is resistant to attack by moths. Dyeing properties are similar to those of wool, although certain dyestuffs have been used also. On small lots using continuous length fiber, woven blends of rayon and cotton have been made as well as knitted fabrics of Sarelon alone and of Sarelon and rayon.

Sarelon produced by the process currently used at the Southern Laboratory has a dry strength of 0.7 grams per denier, a wet strength of 0.2 grams per denier, and wet and dry elongations at break of 11.8% and 22.0% respectively.

In order to obtain light colored protein needed to produce high quality fibers, it is necessary to remove the color in the red skins prior to processing the kernels for oil and meal. One successful method is a process developed at the Southern Laboratory (Patent applied for) which consists of washing the kernel in dilute lye to remove color, rinsing with water to remove excess lye, and drying at room temperature.

Commercial scale production of peanut protein fiber is under active consideration by several industrial concerns.

WESTERN REGIONAL RESEARCH LABORATORY
M. J. Copley, Director

ALFALFA UTILIZATION INVESTIGATIONS

EXTRACTION, STABILIZATION, ANALYSIS OF CHLOROPLAST PIGMENTS
AND OTHER CONSTITUENTS

The Isomers of Carotene

Methods have been developed for rapid harvesting, sampling, freezing, and storing the fresh alfalfa in preparation for analysis. A simple process has been discovered for rapidly extracting the pigments from the plant tissue using polar solvents and transferring them to a nonpolar solvent, which is a necessary step prior to chromatographic analysis.

A method of plotting the progress of the pigments through the chromatographic column has been devised. By its use the relative efficiency of eluants and adsorbants for separating the isomers may be determined. For the resolution of the pigments, hydrated lime was found to be superior to calcium phosphate, aluminum oxide, magnesium oxide, and soda ash. Sharpness of separation of the pigment zones could be improved by the addition of traces of N-propyl alcohol or acetone to the developing liquid during the chromatographic analysis.

Paracresyl methyl ether, a heretofore untried compound, was found to be superior to all the more common eluants studied; one per cent of this ether in Skelly Solve C materially increased the sharpness of separation of the isomers.

These and other modifications and improvements in chromatographic technique for the separation of the carotene isomers show definite promise of making it an accurate and rapid routine analytical method. It will be valuable in research on the extraction of pigments from plant tissues and will have, as well, usefulness in research now under way into means of preserving the biologically active carotene of alfalfa hay through the stages of handling, dehydration and storage.

Spectrographic Determination of Cobalt in Range Grasses

Certain "sicknesses" in cattle have been traced to the lack of minute amounts of cobalt in range feed. Samples of range grasses submitted by the Arizona Agricultural Experiment Station have been analyzed spectrographically for cobalt. The amount of cobalt present was in the order of 0.1 part per million. The results showed conclusively that the lack of cobalt is not responsible for the particular sickness noted in Arizona.

Lipids and Phospholipids

A study on these minor constituents of alfalfa was undertaken to identify the classes present, determine quantities, and to determine if possible their relationship to the degradative changes in the nutrient constituents of alfalfa.

By an acetone precipitation of other extracts, lipid constituents rich in phosphorus have been obtained. Phospholipids and phosphatidic acids appear to be the major constituents of the total lipids. Although considerable work has been done on this subject, the results are as yet only preliminary.

FRUIT UTILIZATION INVESTIGATIONS

FREEZING-PRESERVATION

Prefreezing Treatment of Pie Fruits

During the past year additional information has been obtained, using apricots and peaches as the fruits. It has been found, for example, that in order to give protection against darkening there is an advantage in using a dipping bath containing a combination of sulfur dioxide, ascorbic acid, and salt. By using this combination they exert their desired effect at a much lower concentration than when either is used. The salt concentration was kept at 1.0 per cent, the ascorbic acid from 0.4 to 0.5 per cent, and the sulfur dioxide concentration (added as sodium bisulfite) varied from 300-500 parts per million for peaches, and 800-1000 parts per million for apricots. Since only surface protection is required for peaches, it is more economical to treat large pieces than small ones. In all cases the fruit was held in the dipping bath for two minutes.

Claims have been made that citric acid enhances the effect of ascorbic acid in the prevention of discoloration in fruits. In our tests of this procedure no advantage was observed from the addition of citric acid.

Leaching Losses During Blanching of Peaches

The leaching and weight losses during steam blanching were found to be about 5 per cent of the total solids, which is equivalent to a weight loss of about 1/2 per cent. About 3.5 per cent water was also lost during blanching, giving an overall shrinkage or weight loss of approximately 4 per cent. It was found that there is no significant difference in these losses, whether the peach half was placed cup up or cup down on the blancher belt. This is important from the standpoint of commercial operation since it may permit a saving in labor cost.

Post Blanch Cooling of Peaches

An extensive investigation has been made on this topic. It has been found that in order to reduce the temperature of peach halves to 70° F. (or lower) after blanching and prior to packaging a two-stage cooling process appears to be the logical solution. This two-stage process consists of air cooling, followed by sirup vat cooling. The size of post-blanch cooling equipment for commercial use may be estimated from the information gained in this investigation.

Cold-Processed Gelled Fruit

The effect of various storage temperatures on texture and flavor of the gels has been investigated. It was found that samples stored for three months at -10° F. and lower proved entirely satisfactory. A very slight graininess appeared in some samples stored at 0° F., while $+7^{\circ}$ F. was definitely unsatisfactory. Cooperative work with a commercial producer of jams and jellies is under way, and it is expected that larger-scale trials will be made during the coming fruit season.

High-Frequency Heating at 3000 Megacycles

Work done at this Laboratory showed that radio frequency heating (in the frequency range of 10-50 megacycles per sec.) for the inactivation of yeasts, bacteria, and enzyme was dependent entirely upon the temperatures generated. Studies have been undertaken at 3000 megacycles with a view to determining the conditions for inactivation of yeasts at this frequency. Such conditions should be of especial value in food processing where it is desired to inactivate various organisms and at the same time avoid the use of high temperatures which in many instances cause undesirable flavor changes.

DEHYDRATION

Dehydrofreezing

This name has been given to a combination process in which fruits or vegetables are first dehydrated until $1/2$ to $3/4$ of the moisture is removed, followed by freezing preservation and storage. Work thus far has shown that quality can be fully retained. Some of the advantages are:

- (1) There is a reduction of weight and bulk to approximately one-half that of conventionally frozen foods. This reduction is important from the standpoint that commercial storage and transportation costs are saved, and in the greater quantities that can be stored in the home.
- (2) Freezing costs are less, due to the reduced weight.
- (3) Thawing is much easier and quicker because the dehydrofrozen foods do not form an icy block and will thus break apart readily. Also it is not necessary to thaw before removing a part of the dehydrofrozen food from a large package.
- (4) Reconstitution is quick and easy, and affords an opportunity to introduce supplements or flavoring materials. For example, Delicious apples are low in acidity, making them less desirable as a pie fruit. If fruit acids are added to the water in which such apples are rehydrated,

it will have better penetration than if added to apple slices with a normal moisture content.

Most of the work on fruits so far as dehydrofreezing is concerned has been centered on apples. The reason for this is the great importance of that fruit and the possibility that this new process will be commercially important as a useful supplement to the present methods of supplying fresh and conventionally frozen apples to pie manufacturers. Newtown Pippins from Watsonville, California and common Delicious from Wenatchee, Washington have been the varieties most extensively used in our work thus far, although other varieties have been tried.

Spray Drying

The troublesome problem of sticky mixtures resulting from the drying of fruit juices has been studied. Considerable useful information on required additives and on methods of operation for the drier have been obtained. Work will be continued on this project and it is hoped that results of a more practical nature will be obtained during the present year.

PECTIN

Pilot Plant Production of Low-Methoxyl Pectins

Operation of a pilot plant for the production of low-methoxyl pectin at Chino, California, in cooperation with a commercial concern was begun during the 1946 Valencia orange season. The method included two processes developed at this Laboratory for the purpose of reducing the cost of producing this type of modified pectin. These were: (1) continuous countercurrent leaching of the peel and extraction of the pectin therefrom, and (2) isolation of the low-methoxyl pectin by direct acid precipitation.

The season's run demonstrated the feasibility of the method to produce a high-grade product. It also indicated a number of important facts regarding the kind of equipment needed, the advantages of using dried rather than fresh citrus peel as a source material, and certain advantages to be derived by minor changes in certain of the chemical processes. Included in the latter is the use of sodium instead of ammonium hydroxide as the deesterifying agent with attendant lower chemical costs and neutralization of the dry pectinic acid with sodium bicarbonate instead of ammonia, resulting in better control and no degradation of the low-methoxyl pectin.

Gel Studies

A comprehensive study of factors influencing formation of pectin jellies has been completed. A new and rapid method for measuring the modulus of rigidity has been developed. Such measurements place pectin grading on an absolute rather than a subjective basis. A shear modulus of 3 g./cm² was chosen as standard and this value is being suggested to the

pectin industry. If this standard were adopted, pectin grading should be consistent throughout the industry instead of varying as it now does.

Pectin Analysis

A rapid method for pectin analysis has been developed, which consists in measuring the optical rotation of a solution prior to the precipitation and removal of the pectin, and again afterwards. A complete analysis can be run in less than 30 minutes which makes the method especially valuable for plant control work.

Hydration of Sodium Pectate

The mechanism of hydration of sodium pectate has been studied by the X-ray diffraction technique. The crystallites in sodium pectate sorb a maximum of about 24 per cent water at a relative humidity of 95 per cent at 25° C. The amorphous regions under these same conditions contain over 65 per cent water. The crystallites when maximally hydrated presumably contain alternate water and polygalacturonide chains.

PROTEIN AND VITAMIN-RICH FOOD OR FEED SUPPLEMENTS

Torula Yeast Investigations

Work on torula yeast production from pear waste has gone through its second year of pilot plant investigation in cooperation with the Olympia Canning Company at Olympia, Washington. Feeding tests to evaluate the yeast produced will be continued at the Washington State College Agricultural Experiment Station.

Progress was made toward solving the difficulty of separating the juice from the pear waste prior to fermentation. Additional laboratory work, however, is required on this problem.

The successful demonstration (in pilot plant operations at Olympia) of the feasibility of continuous, automatically controlled fermentation of pear juice represents a further simplification of the process from the commercial standpoint.

ENZYME PREPARATIONS

Polygalacturonase

A simple method has been devised for obtaining high yields of purified polygalacturonase which is needed for studies on the mechanism of juice (especially pear) clarification. The method involves adsorption of the polygalacturonase upon alginic acid with subsequent elution therefrom.

ISOLATION, ANALYSIS, AND CHARACTERIZATION OF CONSTITUENTS

Phase Equilibria Studies

Indications have been obtained that the sucrose-water phase equilibrium diagram at low temperatures is much more complicated than the simple

eutectic picture hitherto believed to be correct.

Phase equilibria in frozen foods have not been adequately investigated, although they are fundamental to freezing, processing and storage. Fundamental information of this kind may ultimately prove to be of practical significance in predicting or understanding the best freezing and storage temperatures for foods.

CITRUS

Amino Acids

The amino acid content of citrus is being studied with reference to their effect on fruit deterioration. The known reactions of amino acids indicate their involvement in the mechanisms of deterioration.

Ethylene Control Experiments

The analytical method for ethylene is based upon using red mercuric oxide which is reduced by the ethylene to form mercury vapor which is in turn detected quantitatively upon selenium sulfide paper. It has been found that scrubbing the atmosphere with 87 per cent sulphuric acid prior to ethylene determination will remove interfering substances such as ethyl acetate, acetaldehyde, ethyl alcohol, acetic acid, ether, acetone, and oil of orange vapor. This procedure eliminates the effects of substances most likely to interfere in analyzing for ethylene in citrus ripening shed atmospheres.

ASCORBIC ACID FROM WALNUT HULLS

Extraction of Hulls

Pilot plant operations were conducted on the production of a walnut hull extract. This was done near Linden, California in cooperation with the California Walnut Growers Association. The countercurrent extraction process proceeded smoothly and no serious difficulties were encountered in operating the equipment. The 3000 gallons of extract obtained have been concentrated at the Western Regional Research Laboratory and are estimated to contain 30 to 40 pounds of ascorbic acid.

Crystallization of Ascorbic Acid

The ascorbic acid is obtained by a process of adsorption on resin ion exchange materials. A method of treating the partially concentrated eluates with activated carbon results in the production of crystalline ascorbic acid. Its preparation in the crystalline form is highly important in that it is now possible to consider its use in all fields where synthetic ascorbic acid is now employed.

POULTRY UTILIZATION INVESTIGATIONS

DEHYDRATED EGG STUDIES

Storage of Acidified Spray-Dried Egg Powders

The beneficial effect of acidification of emulsified whole egg before spray drying on the shelf life of egg powders has been established. The use of acidification in the egg industry as a method of preserving spray-dried powder is indicated, and it is reported already being initiated through the efforts of the Quartermaster Corps.

Lipid Deterioration

Additional data has been accumulated on the mechanism of the deterioration of lipids in dehydrated eggs. Changes in the phospholipid was shown to be heavily involved in the loss of palatability of egg powders.

Egg Enzymes

It has been shown that there is no need to postulate enzyme activity contrary to reports in the literature, in order to explain the formation of free fatty acids in dried eggs.

Yolk Proteins

A new protein component of egg yolk has been found. It is present to the extent of 0.1 per cent, and contains a nitrogen to phosphorus ratio of approximately 3, indicating a phosphate group for every three amino acids. No practical significance of this discovery is immediately apparent, but it adds to the sum of fundamental knowledge available on the subject.

FREEZING PRESERVATION

Prefreezing Treatment and Nitrogen Packing of Chickens to Prevent Oxidative Rancidity of Fat

Fat fowls treated in various ways and then packed and frozen in tin cans have been tested for fat rancidity after 90 days and again after 173 days in storage. Temperatures of 0° and -10° F. were maintained in two similar lots. Lowering the storage temperature to -10° F. seems to be the most effective way for preventing rancidity.

FIBERS, PLASTICS, AND ADHESIVES FROM EGG AND FEATHER (KERATIN) PROTEINS

Cross Linking in Proteins

Fundamental information on the reaction of formaldehyde with proteins has been obtained. It will be of use in determining the optimum conditions for tanning, hardening of protein fibers, etc.

Physical-Chemical Properties

Comprehensive investigations of both the fundamental and practical aspects for the dispersion of feather keratin in alcohol-water mixtures has been carried out. The dispersion of feather keratin by the alcohol method is a relatively simple process which may lend itself to industrial development more readily than previously known method; for example, as a modifier and extender for synthetic resins in the manufacture of a building board. Arrangements have been made with a manufacturer of a board composed of exfoliated obsidian rock to further test those keratins in his product. Study of the application of solubilized feather keratin by the newer technique for bristles, shellac substitutes and adhesives is also being carried out.

Another interesting observation is that the insoluble fraction of feather keratin is digestible by enzymes and could possibly be used as a protein supplement in animal feed.

ISOLATION, ANALYSIS, AND CHARACTERIZATION OF CONSTITUENTS

Trypsin Inhibitor from Egg White

The trypsin inhibitor present in egg white has been isolated and identified. Some physical and chemical properties have been studied. Its inhibitory effectiveness against a number of proteinases has been investigated. Studies are being made of the possibilities of the inhibitor causing growth retardation as has been indicated for the soybean anti-trypsin.

Synthesis of Cephalin

In cooperation with the Enzyme and Phytochemistry Research Division, the starting materials, the intermediates and the final products have been examined by the polarizing microscope during the synthesis of cephalin. The determination of the optical and crystallographic properties provide important fundamental knowledge of the properties of synthetic cephalin as compared with natural cephalin. A further study of this important lipid is thus free from the uncertainty of purity of a product obtained from natural sources and the influence of the unsaturated acids on its behavior is eliminated in enzyme reactions. The results greatly facilitate the synthesis and purification of cephalin.

Fatty Derivatives of Phenothiazone and Thionol

A study has been undertaken in the synthesis of fatty derivatives of the two oxidation products of phenothiazine, phenothiazone and thionol, particularly long chain fatty esters, ethers and acetals of these compounds. The attaining of increased lipid solubility of the ring compounds is the object of this investigation. Products will be analyzed and characterized and such physical and chemical constants determined as may have a bearing on their physiological and pharmacological behavior. Sufficient amounts of each will be synthesized for a study by or through the Pharmacology Division of their pharmacological action, oxidation-

reduction characteristics, fungicidal, bactericidal and anthelmintic properties.

VEGETABLE UTILIZATION INVESTIGATIONS

DEHYDRATION

Moisture Determination of Dehydrated Vegetables and of Fruit Powders

Work has been continued on the establishment of a reference method to calibrate the vacuum oven method for the determination of moisture. The products used included dehydrated potatoes, beets, sweetpotatoes, carrots, and lemon and grapefruit powders. The method can be quickly described as rehydration followed by lyophilization and completion of drying in the vacuum oven. It is simpler and more accurate than those previously used.

Role of Moisture Diffusion in Drying

The factor which limits the rate of drying of cut vegetables is the rate at which residual moisture will diffuse to the surface of the pieces. A mathematical theory has been developed as a guide to further experimental study of this phenomenon. The new theory harmonizes well with hitherto unexplained peculiarities of the drying rates that were actually observed. A simple extension of the same theory is expected to be useful in the study of moisture transmission through sheet packaging materials.

Static Pressure Drop through Bin Driers

An extensive study on this subject has resulted in the development of an equation which will enable future designers of bin driers to predict with reasonable accuracy the static pressure drop in this type of equipment. This information should be quite helpful in the design of such driers which are widely used in the dehydration of vegetables to economically remove the last part of the moisture.

Storage Studies

The experimental part of the comprehensive storage studies on dehydrated vegetables has been completed. That part of the studies dealing with "browning" of dehydrated nonsulfited vegetables was summarized for presentation at the meeting of the American Chemical Society in Chicago. The manuscript on this phase of the study has been submitted to the Society for publication. The results of other phases of the storage studies will be reported in forthcoming manuscripts.

Fluorescence as Palatability Index of Dehydrated Carrots

The results suggest that fluorescence measures a decomposition product which, under some, but not all storage conditions is produced at a rate nearly proportional to the development of undesirable flavors.

Dehydrofreezing

(See also under Fruit Dehydration - this report)

Interesting data have been obtained on the storage (-10° F.) behavior of dehydrofrozen peas. The peas were packed at three different levels of moisture content - 60, 50 and 40 per cent. A comparison series of samples blanched and frozen but undried were also packed. Two types of packages were used, namely, tin cans and cellophane bags. Three different package atmospheres were included - air, nitrogen with 1.5 per cent oxygen, and nitrogen with only 0.5 per cent oxygen.

Taste panel scores indicate that this pack has retained nearly all of its original quality over a five month storage period. None of the various categories of samples has changed enough to warrant conclusions regarding the variables under study, but it appears that inert gas packaging will have no advantages over air. Also the dehydrofrozen peas are equally stable as compared with undried frozen peas.

Dehydrofrozen carrots also compare favorably under storage conditions with those frozen in the normal way. No comparative data, however, are available for gas-packed dehydrofrozen carrots.

FREEZING PRESERVATION

Frozen Sweet Corn

During August 1946, work was conducted at the Davis County Experimental Farm at Farmington, Utah, to compare the quality of sweet corn which has been scalded on the cob prior to cutting with that scalded after having been cut from the cob. This was done to corroborate and extend the investigations made at Prosser, Washington described last year. The conclusion that blanching on the cob gives a better frozen product was confirmed.

Volatile Constituents of Peas

In an attempt to determine the nature of compounds that give rise to off flavors which develop in peas, studies have been started on the volatile constituents. It is expected that this study will be of value in designing objective tests for the determination of quality in both the raw and in processed material.

JUICE CONCENTRATES FROM VEGETABLE WASTES FOR USE IN THE PRODUCTION
OF ANTIBIOTICS AND ENZYME PREPARATIONSSubtilin

An improved method for the extraction and purification of subtilin which has been developed would seem to be suitable for large scale production of subtilin on a commercial scale. The product is of a high degree of purity and a low order of toxicity which seems suitable for therapeutic use.

The fact that medium made from the new asparagus juice concentrate constitutes a good medium for tyrothricin but not for subtilin production (the medium gave excellent B. subtilis cell production) suggests that this concentrate is deficient in an essential nutrient for subtilin formation and hence the problem of fortification of this concentrate will be attacked from this angle. A positive answer to this problem would not only serve as a guide for processing of asparagus waste so as to include this factor or factors but also may lead to the discovery of subtilin precursors.

"Bound" subtilin (the marked increase in antibiotic activity caused by treatment with methanol hydrochloric acid) may be due to the release of subtilin or its chemical alteration either one of which is obviously of importance.

The differentiation of the antifungal and antibacterial activity produced by B. subtilis may lead to a useful by-product of subtilin production as well as a clarification of the conflicting status of the various antibiotics produced by this organism.

Evaluation studies indicate extended scope of possible usefulness of the product in treating human and animal diseases, present new problems regarding methods of administration, and supply additional evidence of antibiotic heterogeneity.

PROTEINS AND PROTEIN COMPLEXES

Browning on Storage

Of the studies involving proteins and protein complexes, that on the browning of protein solutions containing glucose during extensive periods of storage at elevated temperatures is of great interest. Concentrated solutions of sucrose in a browning system will protect the protein from denaturation and inhibit the browning rate in the presence of glucose. This study will be useful in interpreting the different rates of browning observed in vegetables.

Lima Bean Proteins

The enzyme inhibitor of dry mature lima beans has been purified to the point that its activity is at least equal to that of the crystalline tryptic inhibitor from soybean. The purified lima bean inhibitor also inhibits growth in rats but is relatively much weaker for growth inhibition than cruder preparations. The explanation for the discrepancy in activity by the two criteria is being sought.

Guar Bean

A potential source for a mucilagenous or gumlike material would appear to be available in the guar bean, now being grown as a minor crop in Arizona. The milled endosperm has unique colloidal properties and preliminary studies indicate a high degree of commercial usefulness as an emulsifier and thickener in products of the food and pharmaceutical

industries, and as a sizing agent in the paper and textile industries.

Preliminary study, rather limited in scope, suggests that further study of the guar bean is definitely warranted.

Objective Evaluation of Reflectance Color of Vegetables

The influence of reflectance color on acceptability of foods has led to an investigation of the applicability of spectrophotometric methods to objective evaluation of color changes caused by processing procedures. Trichromatic specification is proving applicable to evaluation of these changes, the actual choice of variable depending upon the product and the purpose of the investigation. Further application of these methods is being made in studies of other processing-produced changes such as heat damage in dried potatoes.

WHEAT UTILIZATION INVESTIGATIONS

INDUSTRIAL NONFOOD USES OF GLUTEN

Phosphorylation of Proteins with Phosphoric Acid

Reaction of wheat gluten with phosphoric acid results in the introduction of phosphate groups on the aliphatic hydroxyl groups. The reaction and the properties of the product are analogous to those observed with wheat gluten and sulfuric acid. The sulfating procedure is cheaper, but the phosphate derivative might have unique properties which will make it more useful.

GLUTEN SULFATE

Batch Preparation of Gluten Sulfate

A large enough quantity of this wheat derivative has now been made to permit distribution of generous samples to possible users. This is the first step in determination of possible outlets for the material and the price level at which it would have to be put on the market.

ISOLATION, ANALYSIS, AND CHARACTERIZATION OF CONSTITUENTS

Lipid-Protein Relationship in Gluten

The relationship of lipid to protein in the formation of gluten from wheat flour is being studied in detail. It has been shown that gluten has the capacity to bind more than five times as much total lipid as is originally present in wheat flour. The capacity to bind phospholipid is even greater.

The binding of lipid by flour has been demonstrated with two hard wheat, one soft wheat and one durum (macaroni) varieties. Similar values were obtained in each case.

The demonstration that gluten proteins can bind lipid during kneading even in excess of that present in the flour is of importance in the

technology of baking. It is not generally realized the kneading operation accomplishes a reaction between the protein and the added fats. The fractionation studies are of importance in determining the properties of fat-enriched gluten for possible industrial utilization.

Lipids of Wheat Humins

Samples of wheat humins (residue from the manufacture of sodium glutamate) submitted by two companies showed an oil content of 15.3 and 51.8 per cent, respectively. The ether extract was largely free fatty acids although significant portions (22.5 and 13.3 per cent, respectively) consisted of glycerides. This work indicates that wheat humins are a possible although minor source of fatty acids, particularly of oleic and linoleic acids.

Oil of Pennycress Seed

A preliminary examination of the seed of pennycress has been made. Pennycress is available in the screenings from wheat which in some areas contains appreciable quantities as a weed seed. Tests were run on a sample submitted by the Montana Experiment Station where pennycress seed is being investigated as a possible domestic crop. Proximate analyses indicate that this seed has an oil content of about 34.5 per cent (dry basis) and a protein content of about 21.4 per cent.

The oil is said to be similar to that of rape and mustard seed in its high content of erucic acid, and hence would be valuable in special lubricants.

EASTERN REGIONAL RESEARCH LABORATORY
P. A. Wells, Director

APPLE AND OTHER FRUIT UTILIZATION INVESTIGATIONS

JUICE PRODUCTS

Processing of Apple Juice

During the 1945-1946 season a number of packs of apple juice were prepared, processed and stored under different conditions in an attempt to evaluate the influence on quality of different manufacturing practices, and to determine the most satisfactory method for obtaining a full-flavored and stable juice. The different types of processing used were (1) strained (200 mesh), (2) filtered, (3) centrifuged, (4) enzyme clarified, (5) gelatin-tannin clarified, (6) bentonite clarified, and (7) with added essence.

The most pronounced effect on stability during storage was the effect of temperature. Cold storage very markedly aided flavor retention and also retarded sedimentation in all of the packs. At room temperature storage there was a rather pronounced loss of fresh-flavor in the first two or three months and after that there was little further change. The rate of sedimentation also roughly paralleled the loss of flavor at room temperature storage.

The taste panel showed a definite preference for cloudy juices over the clarified, although the difference was less marked after storage for several months at room temperature. In regard to flavor, there was little to choose between the different methods of preparing either the cloudy or clarified juices. Some sediment separates from the cloudy juices on storage at room temperature, but this sediment does not seem to be as objectionable nor as noticeable as the sediment which separates from the enzyme clarified juices.

Juices clarified with gelatin-tannin or bentonite are more stable as regards sedimentation than the enzyme clarified. The latter deposits considerable sediment on storage at room temperature which is very noticeable in the clear juice. Storage at 35° F. prevented this sedimentation. All methods of clarification involve holding periods and considerably more manipulation than is necessary in the preparation of cloudy juices.

The addition of apple essence to the juice just prior to bottling improved the flavor, especially of the clarified juice. The improvement in flavor is not as marked after several months' storage at room temperature. However, it is believed that the addition of essence may be of definite value, especially in the case of clarified juices.

VOLATILE FLAVOR RECOVERY AND APPLICATIONS

Significant progress has been made in the commercial development of the apple essence recovery process developed here several years ago. At present there are five manufacturers known to be producing fruit

essences for sale. Three of these are producing only apple essence. One of these companies estimates they now have an annual capacity for producing 35,000 gallons of apple essence from the 700,000 gallons of concentrate they are planning to produce from 5,000,000 gallons of juice which is equivalent to approximately 1-1/2 million bushels of apples. Another of the above companies has been producing apple, grape, peach, and cherry essence from a unit with a capacity of approximately 5,000 gallons of juice daily. The most recent company to start production has recovered essences in a relatively small unit from strawberries, pineapples, blackberries, apricots, cherries, and peaches.

In addition to the above, it is understood there are thirteen companies now engaged in the production of the essences from apples, grapes, pineapples, and oranges for use in their own products. Thirty-one other companies have indicated a serious interest in the installation of the essence recovery process and are planning to go ahead as soon as they can obtain the necessary equipment.

Inasmuch as there is such a diversified interest in the evaluation of the process for the recovery of the essence from a large variety of fruits, pulps, and by-products, other than fresh apple juice for which the process had been originally developed, active efforts have been directed toward interesting consultants and equipment manufacturers in the development. As a result, ten consultants and six equipment manufacturers are now actively interested in the solution of problems arising from special applications of this development.

Apple essence has demonstrated its value as a result of numerous industrial evaluation tests and consequently a commercial demand has been created for it as an ingredient in beverages, table sirup, ices, pharmaceuticals, confections, jellies, preserves, gelatin desserts, apple sauce, apple pies, and as a bait attractant.

The present selling price of apple essence is \$15.00 per gallon. The demand is far in excess of supply.

FIRMING OF APPLE SLICES

The soft character of certain varieties of apples has severely limited the methods by which they may be processed satisfactorily, with consequent restriction of commercial outlets. For example, such varieties as McIntosh and Delicious, and all summer varieties, are practically excluded from use in the pie, canning and freezing industries. The development of methods by which such apples and other fruits could be firmed to the proper degree has long been sought by the industry. On the basis of our experience in studies on the preparation and properties of enzyme de-esterified pectin it appeared that a method might be developed through the use of the enzyme pectase. Active work on this problem was undertaken during the past year, and a process was developed which involves introducing a solution of tomato pectase into the apple slices under conditions which cause a modification of the pectin in situ. The resulting slices when baked or otherwise cooked are quite firm.

While these studies were underway, workers at the Massachusetts Agricultural Experiment Station described an entirely different method

in which apple slices were firmed by dipping in a calcium solution. Following the publication of this work informal cooperative studies were undertaken with that Station to compare the pectase and the calcium methods.

Summer and early fall varieties of apples were studied to determine whether they could be adequately firmed by either calcium or a combination of calcium plus pectase. These included Yellow Transparent, Williams, Rambo, Star, Gravenstein, Wealthy, McIntosh, Smokehouse, Jonathan, and Stayman. The laboratory procedure for testing the effect of either calcium or calcium plus pectase was to cover the slices with the desired solution, evacuate the slices to remove air, and then release the vacuum, causing the solution to be forced into the air spaces. This procedure insured uniform distribution of the reacting solution throughout the slices. The slices treated with pectase enzyme were allowed to stand one hour before cooling. The slices were cooked in boiling water for 20 minutes, cooled, and examined for firmness. Five or ten pound lots of firmed slices of each variety were baked into pies at a commercial bakery.

Each of the above varieties when in a firm ripe or slightly immature condition (usual market condition) was adequately firmed with 0.1 to 0.3 percent calcium chloride. For that reason it was difficult to determine if a combination of calcium plus pectase gave any additional increase in firmness. As the apples advanced in maturity the calcium became less effective and higher concentrations were required. With over-ripe fruit calcium did not give adequate firming, but a combination of calcium plus pectase, or calcium plus sodium acetate did give adequate firming.

An attempt was made to develop improved and simplified procedures for applying calcium solutions to apple slices. It was observed that when slices containing the usual amount of air were dipped in a calcium chloride solution, the resulting product was case hardened, or firmed only on the surface. However, if the slices were first evacuated or steamed to eliminate the air in the pores of the tissue, such slices when dipped in calcium chloride solution were uniformly firmed and showed no case-hardening.

Several simplified procedures, suitable for commercial usage, have been developed for calcium-firming apple slices prior to canning or freezing. One commercial apple processor in Michigan recently packed one thousand 30-pound cans of frozen McIntosh slices, using one of the calcium chloride procedures. Two more companies planned to run commercial trials during December, and several others have made plans to put up large packs of calcium firmed slices at the start of next season.

VEGETABLE UTILIZATION INVESTIGATIONS

LEAF PROTEINS AND OTHER CONSTITUENTS

Antibiotics from Onions

In cooperation with the Michigan Agricultural Experiment Station studies on antibiotics from onions were undertaken during the past year.

Using dehydrated garlic powder supplied by the Michigan workers as a standard of antibiotic activity against Phytomonas phaseoli and other gram negative organisms, it has been possible to test the activity of numerous onion preparations in an endeavor to find methods of concentrating and isolating the antibiotic substance or substances present in certain varieties of onions.

Various methods of drying onions were tried as well as methods of extraction of fresh onions and onion juice. Air drying, either in a tray or drum drier, resulted in an almost total loss of antibiotic activity even at temperatures as low as 140° F. Vacuum oven drying yielded a product with slight activity and vacuum drum drying gave a product of low activity when the product was still tacky and no activity when completely dried.

Since all conventional methods of drying onions or onion juice caused practically complete destruction of the antibiotic principle present in the fresh material, the method of drying from the frozen state was tried. By this procedure it was possible to dry onion juice and retain the antibiotic activity to a partial extent. Since even this method destroyed about two-thirds of the activity it seems impractical for large scale use. Solvent extraction with a liquid-liquid extractor can be used to obtain a concentrate in the form of an oil which has about eight times as much activity as the original juice.

Extraction of the wet material seems indicated but its large scale application may be difficult since preliminary pilot plant studies have already indicated that the fresh onion slurry is a very irritating and disagreeable product with which to work even on a moderate scale.

AMINO ACID ANALYSIS OF VEGETABLE LEAF PROTEIN CONCENTRATES

The amino acid contents of vegetable leaf meals and protein concentrates prepared from vegetable leaves by fermentation with Clostridium roseum and by formic acid extraction are being determined by the microbiological procedure of Stokes. From the results obtained so far it appears that the vegetable proteins are similar in their amino acid contents and appear to be good sources of most of the ten essential amino acids determined.

RUTIN

Agronomic Studies

Experiments in cooperation with the Pennsylvania Agricultural Experiment Station and the Bureau of Plant Industry, Soils and Agricultural Engineering were performed last summer to determine the effect of fertilizer treatment on two species of buckwheat. Of the two species, Tartarian (Fagopyrum tataricum) and Japanese (Fagopyrum esculentum), the Tartarian was superior to the Japanese, both as to percentage of rutin and total yield per acre. In addition, the rutin content did not begin to diminish as early as in the Japanese and, therefore, the date of harvest is not so critical. On the soil studied, the results obtained indicate that the application of phosphorus alone produces greater increases in the rutin content than does application of phosphorus and potassium; or nitrogen, phosphorus and potassium.

Analytical Studies

An ultraviolet spectrophotometric method has been developed for determining rutin in partially purified preparations and in pharmaceutical tablets. The method involves measurement of the ultraviolet absorption of 95 percent ethanol solutions at two wave lengths to determine rutin and its aglycone quercetin, and measurement of absorption of ethanol solutions at five wave lengths in the visible spectrum in order to detect the presence or absence of chlorophyll and the red pigment of buckwheat. The method is extremely sensitive and well adapted for establishing the purity of rutin for pharmaceutical use.

Clinical Testing

Two exhibits presented at meetings of the American Medical Association, as well as several new publications on the clinical use of rutin, have appreciably widened medical interest in this drug during the past year.

Clinical testing in cooperation with physicians has been continued. As a result of interest aroused in medical circles on the subject of rutin, an additional number of physicians have requested rutin for use in their practices. A paper by Dr. Ralph L. Shanno of Wilkes-Barre, Pennsylvania on "Rutin: A New Drug for the Treatment of Increased Capillary Fragility" was published in the American Journal of Medical Sciences for May 1946. Drs. Griffith, Lindauer, Shanno and Couch presented a scientific exhibit on the medical applications of rutin at the San Francisco Meeting of the American Medical Association, July 1 to 5, 1946. The incidence of increased capillary fragility in hypertension, effect of therapy with thiocyanate and relation to the hemorrhagic complications of apoplexy and retinal hemorrhage, and the result of treating such persons with rutin, including effect on blood pressure and symptoms and comparison of results with hesperidin, were demonstrated. More than 2,000 copies of this exhibit have been distributed to interested physicians. The exhibit was honored by receiving a certificate of award from the committee of the American Medical Association. A similar exhibit presented before the Pennsylvania State Medical Society in Philadelphia, October 7-10, 1946, by Drs. Griffith, Shanno and Lamott was awarded second prize.

A paper on the use of rutin in the treatment of hereditary hemorrhagic telangiectasia was published by Dr. S. D. Kishlan of the Yale Medical School. It was demonstrated that bleeding from the intestines, nose and gums was promptly arrested by administration of the drug.

Dr. M. I. Plungian of Temple University School of Pharmacy has prepared a paper describing preliminary studies on the coagulation of the blood of rats brought about by rutin, especially in the presence of bile salts. Dr. Plungian has found that rutin decreases the coagulation time of the blood but the effect is not apparent for 3 weeks. When bile salts are given simultaneously the effect appears in 24 hours. The opposite action of dicumerol is antagonized by rutin, especially in the presence of bile salts. Members of the laboratory staff collaborated with Dr. Plungian in this work.

Commercial Production

A number of companies produced rutin on a manufacturing scale during the past summer. Included among these are: The Abbott Laboratories; Parke, Davis & Company; E. R. Squibb & Son; The Maltine Co.; New York Quinine & Chemical Company; Sharpe and Dohme; S. B. Penick and Company; Wm. S. Merrell Company; J. T. Baker Chemical Company; The Medical Products Company. Total rutin production in 1946 is estimated at 10,000 pounds.

Tablets of rutin have been placed on the market for retail sale by The Abbott Laboratories and E. R. Squibb & Son. Indications are that at least four other companies will shortly follow suit.

The Laboratory has actively cooperated with commercial producers. Repeated conferences have been held with members of their technical staff, studies have been made on the large-scale drying of buckwheat by commercial driers, and close association has been maintained with chemical firms that are producing rutin from buckwheat.

TOBACCO UTILIZATION INVESTIGATIONS

RECOVERY OF NICOTINE FROM TOBACCO

During the past season attention was directed to certain processing problems which would be involved in the use of Nicotiana rustica for the production of nicotine. Studies by the Department's Bureau of Plant Industry, Soils and Agricultural Engineering have shown that nicotine yields from Nicotiana rustica under irrigation amount to 150 to 300 pounds per acre, whereas in rain areas less than one hundred pounds are usually obtained. Since there are no nicotine extraction factories in the growing areas most favorable for this type of tobacco, studies were undertaken to determine whether it would be feasible to recover nicotine from the fresh plant in new factories located in the proper growing area, or whether drying and shipping the tobacco to existing extraction facilities would be preferred.

In cooperation with the Bureau of Plant Industry, Soils and Agricultural Engineering, plots were grown at Wyndmoor, Pennsylvania; Beltsville, Maryland; Transon and Waynesville, North Carolina; Greeneville and Springfield, Tennessee; and, in addition, at two points in Alaska by the Alaska Experiment Station. The Alaskan studies are of importance since if it is feasible to produce the crop in that territory, it would give Alaska an exportable agricultural crop which does not now exist. The crop could be processed on the spot and the concentrated product exported in steel containers.

The yields of nicotine secured at Wyndmoor ranged up to 240 pounds per acre. Since the field work was arranged to meet the daily requirements of the laboratory and the pilot plant for material, it was not practical to handle the field work so that maximum acre yields could be secured as would be done where the agronomic features were the first concern. However, the matured lots of tobacco used during the season yielded at rates above 200 pounds of nicotine per acre.

The green weight of the matured tobacco harvested at various times and calculated to a full field stand of 10,000 plants per acre yielded about 28,000 pounds, or 4,200 pounds dry basis. This includes the entire plant of leaves and stalks. These yields were secured in a field of only medium fertility.

The nicotine content of various samples is regarded as normal. While some of the leaf tissue analyzed fairly high, up to 12.4 percent, the average nicotine content of the whole harvested plant (stalk and leaves) is of first importance. Reasonably large lots of plants harvested for the pilot plant studies and in which leaves and stalks were used, ranged in nicotine content from 5.33 to 6.79 percent on a moisture free basis. This is considered well within the range of "good" yields. Data from the remaining plots are not yet available.

Distillation of Nicotine

Experiments carried out in the pilot plant, using whole fresh rustica plants of between 1.6 and 6.8 percent nicotine content, showed that nicotine can be recovered from them in good yield by a comparatively simple process. The fresh plants were reduced to a slurry by passage through a hammermill equipped with a screen having holes one-half inch in diameter. This slurry was then charged into a cylindrical vacuum drier equipped with an agitator. Lime was added to the mixture to release the nicotine and it was then distilled at atmospheric pressure. Ninety to ninety-five percent of the nicotine in the plants was recovered in the distillate. The concentration of nicotine in this distillate was about 0.8 percent, as compared with 0.6 percent in the distillate usually obtained in the commercial processing of tobacco stems.

Attempts to obtain higher concentrations of nicotine in the distillate by the use of various combinations of vacuum and atmospheric distillation were not successful in that, although some of the nicotine was recovered in a more concentrated form, the overall recovery was low.

Metal Nicotine Salts and Nicotinium Salts

Insecticidal evaluation of a number of metal nicotine salts and nicotinium salts was conducted in cooperation with entomologists at the Connecticut Agricultural Experiment Station. Laboratory tests on an extensive series of nicotinium salts against Aphis rumicis indicated that only those compounds having a dinitrophenyl group were more toxic than the nicotine sulfate controls. Didodecyl nicotinium dithiocyanate, however, exhibited a steep dosage mortality curve and approximated nicotine sulfate in toxicity in the high mortality range. Zinc nicotine thiocyanate was evaluated in field tests against the Oriental fruit moth in Elberta peaches. Spray applications containing no wettable sulfur were more effective than comparable sprays containing sulfur. The zinc nicotine thiocyanate sprays gave fair control of the Oriental fruit moth but were less effective than DDT-sulfur dusts.

Field tests against the cabbage maggot on radishes were conducted in cooperation with the Pennsylvania Agricultural Experiment Station. Cupric dinicotinammino fumarate was found to give good control but was inferior to DDT.

The fungicidal evaluation of nicotinium salts was continued in cooperation with the Rhode Island Agricultural Experiment Station. Attempts were made to improve toxicant retention under field conditions. Preliminary laboratory tests indicated that abietic acid and 2-naphthol-6-sulfonic acid were most effective of the twelve acidic materials formulated with dodecyl nicotinium bromide.

Nicotine-DDT

Results of field tests against the European corn borer with nicotine bentonite-DDT mixtures were reported by cooperating entomologists at the Connecticut Agricultural Experiment Station. No definite, unequivocal evidence of synergism was shown in these tests, although mixtures containing 3 parts of nicotine bentonite and 1 part of DDT were slightly more effective than other ratios of the toxicants.

MILK PRODUCTS UTILIZATION INVESTIGATIONS

MILK PROTEIN STUDIES

Bristles from Milk Proteins

The method for making casein bristle has been further developed. Special equipment was designed and constructed which solved the difficult problem of continuous operation of the hardening and drying steps. As a result the entire process can now be accomplished in a wholly continuous manner. This has resulted in improvement in the quality of the fiber, particularly as regards flexibility. Based on our experience in the development of the process, assistance was rendered in the establishment of a new factory at Salisbury, Maryland for the commercial manufacture of casein bristle. This factory, which was formally opened on November 25, 1946, is owned by the Rubberset Company and manufactures both fiber and brushes. It is expected that casein bristle brushes will soon be on the market.

Structure of Proteins and Protein Fibers

An important phase of the utilization investigations on milk by-products is concerned with basic studies on the separation, purification, analysis, structure, chemical modification and other reactions of the protein components of milk. Information derived from such work is frequently essential in the solution of various practical utilization problems. For example, by controlled experiments we are determining the contribution of the various groups present in proteins to their water absorbing properties. These studies are essential to an understanding of the properties of protein fibers, and they tell us what maximum effects can be expected from the blocking of any particular group by chemical modification.

During the past year studies of vapor phase absorption of water by proteins and model substances have given interesting results upon a series of glycine peptides. Both the di- and tri-peptides, which are definitely non-hydroscopic, and the higher members of the series, which show the major characteristics of water absorption of proteins, have only amino, peptide, and carboxyl groups. There are indications that

the contribution of the latter is negligible, and in benzoyl tetraglycine the peptide group alone probably accounts for the observed effects.

Molecular Weight of Lactoglobulin

Considerable interest has been aroused recently in the determination of high molecular weights by the light scattering method of Debye. We have developed an improved apparatus for applying this method to proteins and other high molecular weight materials. The apparatus comprises a sensitive photoelectric photometer for measuring the light scattered by dilute solutions, and a differential refractometer for measuring the refractive index difference between a dilute solution and a pure solvent. Both quantities are required for a determination of molecular weight. The light scattering method has the advantage of rapidity as compared with other methods. This is especially important in the case of proteins since denaturation with time is likely to occur. Another feature of the method is that denaturation can quickly be detected and followed by light scattering measurements. A value of 30,000 has been obtained for the molecular weight of beta-lactoglobulin on the above-mentioned apparatus. The uncertainty of this determination is conservatively estimated as 15%. This result compared favorably with values reported in the literature, which range from 33,000 for wet crystal X-ray data to 42,020 for chemical analysis.

Amino Acid Composition of Alpha- and Beta-Casein

The isolation of two mutually distinct components from casein, recently reported from this Laboratory, has made it important to investigate their comparative amino acid composition. Noteworthy differences have already been revealed. In the following sets of values each figure denotes the average of replicate analyses for whole casein, alpha- and beta-casein respectively, the amino acid contents being expressed as grams yielded by 100 grams of dry ash-free protein; lysine, 8.1, 8.9, 6.6; arginine, 4.1, 4.3, 3.4; histidine 3.1, 2.9, 3.1; tyrosine, 6.3, 8.1, 3.2; tryptophane, 1.3, 1.7, 0.5. The histidine content of the fractions appears to be the same within the limits of experimental error but the other amino acids thus far investigated are present in appreciably higher amounts in alpha-casein than in the beta fraction.

CARBOHYDRATE STUDIES

Resin and Elastomer Intermediates, Plasticizers and Solvents from Lactic Acid

The supply of plasticizers is seriously inadequate for the growing needs of the plastics and elastomer industries, and it is expected that this condition will continue for at least two or three years. Vinyl chloride polymers and copolymers will require the largest volume of plasticizers, but large quantities will be used also with materials such as cellulose acetate, ethyl cellulose, nitrocellulose, polyvinyl butyral, and nitrile rubbers. It is estimated that over 200,000,000 pounds of plasticizers, commanding prices as high as \$1 per pound, will be needed for vinyl chloride resins alone in 1947. It is of interest to compare the volume of plasticizers (200,000,000 pounds for vinyl

chloride resins alone) with the total annual production of lactic acid, i.e., about 6,000,000 pounds.

In view of this situation and the ease with which lactic acid can be converted into derivatives having many of the properties required in plasticizers (such as low vapor pressure, compatibility with commercial resins, and water insolubility), considerable attention has been given to the development of plasticizers from lactic acid. Distillation methods were not employed to purify certain of the lactic acid plasticizers because of high molecular weight and in the interest of economy. The undistilled products, however, were adequately refined by washing with alkaline solution and decolorized with activated carbon.

Polylactic Acid Esters

During the past year studies on the preparation of a new class of lactic acid derivatives was undertaken. These new compounds are esters of polylactic acid which have considerable potential usefulness as plasticizers for certain types of polymers. Preparation of the polylactic acid esters is accomplished by heating a lactate ester in the presence of a suitable esterification catalyst. In the case of methyl lactate, for example, methyl polylactate is produced along with methyl alcohol. By continuous removal of the alcohol favorable displacement of the equilibrium is effected, resulting in excellent yields of the polylactate ester. In this manner methyl, ethyl and butyl polylactates having an average of 3 to 5 lactic acid units in the polymer were prepared. By appropriate treatment these esters can be converted to the corresponding acetate, propionate, etc.

Because of the low vapor pressures of the polylactates, purification by distillation has not proved feasible. They may be decolorized, however, by treatment with activated carbon. The esters thus decolorized, although not chemically pure, are almost colorless, essentially neutral esters. The evaluation of these materials as plasticizers is incomplete, but the compatibility of methyl acetyl polylactate and butyl acetyl polylactate with vinyl chloride-acetate copolymer and ethyl cellulose has been demonstrated.

Plastics, Adhesives, Coatings and Elastomers from Lactic Acid

Acrylic Rubber: The superior resistance of Lactoprene EV vulcanizate to heat was reported last year. This outstanding performance, however, is limited to dry heat and does not include exposure to steam or hot water. Usually Lactoprene EV vulcanizates increase in volume by 100 percent or more when immersed in steam for several days. An important application for heat resisting rubbers is the material for curing bags used in the manufacture of automobile tires. Present tire manufacturing methods require that the curing bag be capable of withstanding repeated exposure to live steam at temperatures in the neighborhood of 310° F. Because of the possibility of utilizing Lactoprene EV in this field, steam and water resistant formulations were investigated.

It was found that the use of certain metal oxides, specifically zinc oxide, lead oxide, and magnesium oxide, as fillers in lactoprene black stocks improved the water resistance of the vulcanizate.

Combinations of zinc oxide and magnesium oxide are most effective in this respect, and appear to be preferable to combinations containing lead oxide. The lead oxide is objectionable because it causes further curing of the vulcanizate at elevated temperatures. Further improvement in water resistance is being sought.

ANIMAL FATS AND OILS UTILIZATION INVESTIGATIONS

PROCESSING STUDIES

Further progress has been made in the studies of hydrogenation as a means of improving the physical properties and of increasing the stability of lard. Through examination of samples representing successive stages in hydrogenation of lard to stearins, it was found that the stability toward oxidative rancidity increased proportionally to the decrease in linoleic acid content. When linoleic acid (as glyceride) had been nearly completely hydrogenated, principally to oleic and iso-oleic acids, the stability increased rapidly. On further hydrogenation, the stability increased proportionally to the decrease in oleic acid content. Finally, when the iodine value of the sample had been decreased to about 20, at which point probably nearly all normal oleic acid had been hydrogenated, further hydrogenation proceeded more slowly and there was another sharp increase in stability. During this final stage the increase in stability seemed to be related to the decrease in iso-oleic acid content.

The percentages of tri-, di- and mono-saturated and tri-unsaturated glycerides of the original lard and of the samples of lard hydrogenated to successively greater degree were determined. In the early stages of hydrogenation the amounts of tri-saturated and di-saturated glycerides increased, resulting in corresponding decrease in mono-saturated glycerides. During the later phase of hydrogenation, after nearly all the linoleic acid had been hydrogenated, tri-saturated and di-saturated glycerides increased at a faster rate owing to reduction in tri-unsaturated as well as mono-saturated glycerides.

STABILITY AND STORAGE INVESTIGATIONS

Studies concerned with the synthesis and evaluation of various new compounds as antioxidants for fats have been continued. Greatly improved yields were obtained by use of a hydrogen bonding agent, which overcame the interference of hydrogen bonding with the normal esterification of gallic acid and the higher alcohols. By this procedure pure lauryl gallate has been prepared in yields of 70-80 percent.

The antioxidant properties of these various compounds are being tested by the active oxygen stability test and by baking tests. The baking tests are used to determine the power of the antioxidant to protect the fat in baked products. Tests to date indicate that the higher gallate esters compare favorably with the best of antioxidants which are used in animal and vegetable shortenings.

Information on initial oxidation products of polyunsaturated fatty acids was obtained. Spectrophotometric data indicate that, on storage in the presence of air, linoleic and linolenic acids undergo autoxidation,

producing compounds which on heating have one more double bond than the initial acid, and these double bonds are conjugated.

PLASTICS, PLASTICIZERS, COATINGS AND OTHER INDUSTRIAL CHEMICALS

When 9,10-epoxystearic acid is reacted with allyl alcohol, allyl allyloxyhydroxystearate is produced. When this compound is copolymerized with vinyl acetate it yields insoluble clear colorless polymers which range in physical appearance from hard and glass-like to soft and rubbery. Polymers prepared from allyl esters, such as diallyl phthalate, are a relatively new class of polymers which approach glass in surface hardness. Since it has been demonstrated that the widely-separated allyl groups in allyl allyloxyhydroxystearate are both capable of entering into copolymerization reactions, this compound may be a valuable addition to the list of active monomers for use with diallyl phthalate, etc., to give modified copolymers having industrial utility.

Vinyl oleate, furfuryl oleate and oleyl oleate have been prepared in good yield from pure oleic acid by relatively simple methods. The products are colorless and odorless, high-boiling liquids. These esters, as well as beta-chloroallyl oleate and methallyl oleate, were also copolymerized with vinyl acetate to yield, with the exception of furfuryl oleate, clear, insoluble colorless polymers which are similar in physical appearance to the allyl vinyl acetate copolymer described above. Furfuryl oleate yielded a soluble polymer.

The fact that the esters of oleic acid described above yield insoluble polymers when they are copolymerized with vinyl acetate indicates that the 9,10-double bond in these compounds can be activated so as to be reactive in copolymerization reactions. It should be possible, therefore, to copolymerize oleic acid, and compounds structurally related to it, with other active, unsaturated monomers, such as vinyl chloride, styrene, acrylic acid derivatives, etc., which are commercially available and used in large quantities. By such a reaction, the fatty acid chain can be made an integral part of the polymer molecule and should impart very interesting and valuable properties to the finished product. Since the fatty acid chain would be actually combined chemically in the polymer and the double bond would no longer be present, relatively permanent plasticization and polymer modification should be attainable. This use for oleic acid and related products represents a potentially large outlet for fats.

POTATO UTILIZATION INVESTIGATIONS

TECHNOLOGY OF POTATO STARCH

Storage and Quality Studies

Work undertaken in cooperation with the Maine Agricultural Experiment Station to determine the influence of storage conditions on the starch content and the yield and quality of starch from potatoes was completed. Green Mountain and Katahdin potatoes, the two leading varieties grown in Maine, were stored at various temperatures ranging from 34° to 60° F. Samples were removed periodically for analysis and starch recovery tests during a total storage period of 37 weeks.

The most important chemical changes occurring in potatoes in storage from the point of view of industrial or food uses are those in starch and sugar contents. The results indicate that relatively large increases occur in the total sugars (primarily in reducing sugars) of potatoes stored at 34° and 36° F., the greatest increase occurring in the first 13 weeks of storage. At storage temperatures of 38° and 42° F. the increase in both total and reducing sugars was slight, and at temperatures of 50° and 60° F. the total sugar contents showed a slight reduction. Parallel with the rise in sugar values there was a corresponding decrease in starch content.

These results were obtained in potatoes analyzed immediately on withdrawal from storage. If, however, the potatoes after withdrawal from storage are kept at room temperature for two weeks or longer, the sugar contents (both reducing and total) gradually diminish, while a corresponding increase in starch content takes place. Green Mountain varieties showed this trend to a more pronounced degree than the Katahdin variety. Both varieties of potatoes stored at temperatures between 34° and 50° F. lost 4 to 6 percent in weight during the first five months of storage, while at 60° F. weight losses of 10 to 11 percent were incurred. This loss was not due primarily to evaporation of moisture. The percent of moisture in all samples stored at various temperatures and for various periods of time did not vary much more than one percent, and in some cases there was even an increase in moisture content. It appears that most of the loss of weight in stored potatoes is due to metabolic changes.

The data on changes in starch and sugar content of potatoes during the cold storage and post-storage periods demonstrate that neither the starch manufacturer nor the potato dehydrator should use potatoes immediately after withdrawal from cold storage. The former will get a low yield of starch due to the presence of large amounts of sugars, and the latter will get an inferior product due to the large amount of reducing sugars present.

From the viewpoint of industrial utilization it was important to determine if storage affects the physical properties of and the ease of recovery of the starch. Accordingly, starch was prepared from potatoes stored for various periods of time and at different temperatures. No differences in the ease of recovery or in the quality of the starch (based on hot-paste viscosity measurements) were observed over the original potatoes before storage.

Analysis of Starch Factory Operations

Basic information on potato starch manufacturing operations was obtained through a detailed study of materials balance in two Maine starch factories. One of these represented the so-called modern type, which uses improved methods of washing and grinding the potatoes, screening of the pulp, protein water removal, separation of impurities and settling of the starch. The other was representative of the vat-settling process factory in which the protein water and other impurities are removed during the starch settling which takes place in large concrete vats.

A yield of 71.3 percent of the available starch was obtained for one day's grinding in the vat factory as compared with 84.5 percent for

the modern factory. The amounts of starch lost in the waste pulp and in the removal of protein water were about the same in each factory. The lower yield in the old-type factory was due mainly to the loss in brown starch, which amounted to 16 percent as compared to 2.2 percent in the modern factory.

Study of protein balance showed that more than 80 percent of the original protein was discharged in the protein water either by vat drainage or by centrifugal separation. The remaining protein was found principally in the waste pulp. The waste pulp from the vat factory contained 4.1 percent solids, of which 43.9 percent was starch; the waste pulp from the modern factory contained 2.7 percent solids, of which 41.5 percent was starch. The waste products from the vat factory (pulp, protein water, and brown starch) contained (on the dry basis) 28 percent protein, 45 percent starch, and 27 percent other constituents (mainly fibrous material). The waste material from the modern factory (pulp, protein water, and table tailings) contained 32 percent protein, 24 percent starch, and 44 percent other constituents. The difference is mainly due to the high starch loss in the brown starch of the vat factory.

The basic data obtained in this study will serve as a guide for future experimental work on (a) improvements in the technology of potato starch manufacture, and (b) recovery and utilization of starch factory waste products. A pilot plant unit is now being assembled which will permit independent study of each processing operation

STARCH ESTERS AND ETHERS

Preparation and Evaluation of Allyl Starch

In view of the wide industrial interest in allyl starch, every effort has been made to perfect a practical and economical method of preparing this material. Much experimental work has been carried out in order to overcome some of the difficulties encountered, and several practicable methods have been developed which yield products that give satisfactory films if properly formulated. Pilot plant equipment for preparing allyl starch has been designed based on laboratory results, and an order placed for the equipment. As soon as this equipment is received, large-scale batches of allyl starch will be prepared, which should afford ample opportunity for more complete and final evaluation of both the method of preparing allyl starch and its application as an air-hardening protective coating. It should be pointed out that the performance of allyl starch as an air-hardening coating is dependent not only on preparation but on such variables as solvents, modifiers, peroxide content, and possibly molecular weight. A number of commercial concerns are actively interested in the manufacture of allyl starch, and complete information on the methods of preparation developed by the Laboratory has been supplied them. It is our understanding that one large company is setting up pilot plant facilities for manufacturing allyl starch.

Influence of Moisture Content on the Keeping Quality of Potato Starch.

It has been reported that potato starch undergoes serious deterioration on storage at room temperature for as little as five months.

Because potato starch is normally produced with a high moisture content, about 17 percent, it was thought that this might be the important factor in determining the rate of deterioration. To test this, portions of a sample of potato starch were adjusted to moisture contents of 5, 10, 15, 20 and 25 percent, and stored at 25° C. for eight months. The viscosity of a 3.5 percent paste of each was then measured. No great changes in viscosities were found, indicating only minor quality deterioration in the starch. Viscosities measured after storage were slightly higher, whereas it has been reported by Katz (Textile Research 9, 69 (1938)) that they should be only a fraction of those initially observed. These results indicate that potato starch can be stored for several months at room temperature with moisture contents varying from 5 to 25 percent without undergoing significant deterioration.

TANNING MATERIALS, HIDES, SKINS AND LEATHER INVESTIGATIONS

DEVELOPMENT OF NEW AND POTENTIAL TANNING MATERIALS

Canaigre

Because of the considerable promise of canaigre as a source of vegetable tannin, it was felt desirable to secure at least 100 tons of roots to permit extensive pilot plant scale extraction work and to obtain sufficient canaigre tannin for commercial tanning tests. Efforts to obtain this supply from wild roots in Arizona during the past summer were unsuccessful. However, as an initial step in semi-commercial canaigre growing, a small field was planted in October 1946 near Lordsburg, New Mexico, through the cooperation of the Lordsburg Chamber of Commerce. It is hoped that this, together with roots obtained from plots at Winter Haven and Lubbock, Texas, and State College, New Mexico, will supply a major part of the material needed for large-scale extraction and tanning tests.

Studies on the propagation of canaigre by planting seed have shown that canaigre propagated in this manner and allowed to grow for three years before harvesting gave a total average yield of 34 tons per acre, or an equivalent of 11.3 tons per acre per year. The canaigre roots, produced after three years of growth from seed, showed an average tannin content of 21.3 percent and a purity of the water extractives averaging over 50.

Preliminary work has been started on the pilot-scale extraction of canaigre. In these tests the shredded roots were pulped in a pebble mill, centrifuged to separate the liquor, and the solid matter mixed with water and again centrifuged. It was found that two-thirds of the sugar present in this liquor could be removed by 24-hour fermentation with Aerobacter aerogenes, resulting in a substantial increase in purity of the tannin solution.

Studies are also underway in the pilot plant to determine the best method of preparing the roots for leaching consistent with rapid de-watering between leaches and elimination of suspended solids prior to fermentation of the extracts.

Sumac

Progress has been made in the development of high tannin strains of sumac in plantings at Beltsville, Maryland which should be suitable for use in establishing small commercial plantings. Further progress has been made in comparison of leathers tanned commercially with Sicilian and American sumacs to demonstrate whether American sumacs can be successfully used to replace the imported Sicilian sumac. Extensive data accumulated by the Laboratory on the composition of domestic sumacs have been assembled for publication as a Department Bulletin.

Scrub Oak

Progress has been made in the development of scrub oak bark as a source of tannin. This work is being conducted in cooperation with the Engineering and Industrial Experiment Station of the University of Florida.

The proposed method of producing scrub oak bark involves chipping of the logs and branches followed by a mechanical separation of the wood and bark. A number of methods were tested unsuccessfully, but it was finally demonstrated that a commercially available machine combining vibration with air levitation effected a satisfactory separation of the materials, provided the wood-bark mixture was dry enough to flow readily on the vibrating air-float table. The use of this machine will solve the principal technical difficulty in the field.

This work has progressed to the stage at which field operations could be started, but is being delayed by difficulties in financing and securing the necessary equipment. Our cooperators estimate that when the equipment is acquired and ready to operate, about two weeks will be required to cut the wood and process the 200 tons of bark needed for large scale extracting and tanning tests. If the project proves successful, this development may play an important part in meeting the urgent need for increased supplies of domestic tannins.

Pecan Shells

Although the tannin from pecan shells is now being recovered and used to a limited extent in tanning, a systematic study of the separation of the shell liners and recovery of this tannin has not been made previously. Preliminary work on this problem involving analysis of hand separated inner and outer shell liners from three improved varieties revealed that the outer liner contains less than one percent tannin, whereas the inner liner contains from 25 to 39 percent. While the amount of pecan tannin potentially available is small as compared with the total domestic tannin consumption, it nevertheless represents a substantial quantity, which we estimate at 3,000 tons annually.

DEVELOPMENT OF COMBINATION VEGETABLE-ALUM AND OTHER TANNAGES

Investigations looking toward the development of more serviceable insole leathers in cooperation with the War Department were continued. On the basis of previous tests, it is believed that improved durability of insoles may be secured by increasing the amount of Al_2O_3 fixed in alum retanned vegetable leather. The tests conducted have sought to

obtain an Al_2O_3 content greater than three percent, a more uniform distribution of Al_2O_3 throughout the cross-section of the leather, and a shortening of the time required for processing.

Last year it was reported that increased fixation of Al_2O_3 may be accomplished by use of a mixture of sodium tartrate and sodium acetate as "masking" agents in the alum liquor and it was believed that the tartrate was the main "masking" agent. However, it has now been definitely established that sodium acetate alone is at least as effective as when used with sodium tartrate. This is important since it permits a substantial reduction in cost of the treatment.

Tanning solutions containing 20 percent sodium acetate, based on the weight of Al_2O_3 , when used for retanning vegetable tanned sole leather bellies, gave in every case Al_2O_3 contents above three percent when tannage was continued over a period of one week.

When subjected to the boiling test, some leathers, even though containing more than three percent Al_2O_3 , showed a dark streak with shrinkage at the center between flesh and grain. This indication of uneven distribution of Al_2O_3 was confirmed by analyses of the leather split into three sections - grain, interior, and flesh. Although it is quite possible that protection of the surface layers would be sufficient for insole leathers, nevertheless, attempts are being made to secure more uniform penetration and also to shorten the time required for retannage.

IMPROVED CURING METHODS FOR HIDES AND SKINS

Basic data are being obtained on the strength of skin before and after certain treatments. The data will be of value not only in our studies of the effect of hide curing agents on the strength of leather made from specially cured hides, but also in studies on tanning agents. With present shortages of hides and leather, effective curing methods that prevent unnecessary hide losses are important.

In studies on the effect of chemicals added to salt for curing hides or skins, one of the best mixtures found was salt containing 0.1 percent of its weight of paranitrophenol and 1.0 percent of sodium silicofluoride. In tannery trials, however, leather produced from hides cured with this mixture was slightly but definitely weaker in tensile strength (5 to 8 percent) than leather from hides cured with salt alone. The tannery results were obtained in three tanneries using entirely different types of tanning agents and skins. In our laboratory tests, pieces of hide were cured with salt containing (1) paranitrophenol, (2) sodium silicofluoride, and (3) both of these chemicals. The resulting leathers showed no differences in tensile strength due to chemicals added to the salt. This result is at variance with the tannery tests. Before testing, the leather was pressed at 2,000 pounds per square inch for 3 minutes to simulate the rolling applied to sole leather. To determine whether the pressing had altered the tensile strength values, the experiment was repeated, half the tanned pieces being pressed as before and the remaining pieces being pressed only enough to flatten them. Preliminary examination of the test data reveals no differences in strength due either to pressing or to curing treatment.

NORTHERN REGIONAL RESEARCH LABORATORY
G. E. Hilbert, Director

AGRICULTURAL RESIDUES UTILIZATION INVESTIGATIONS

COMPOSITION AS AFFECTED BY VARIETY, BREEDING, ENVIRONMENT, AND MATURITY

Analysis of Stalks of Flint and Dent Type Corn

Cornstalks representing flint and dent types of corn were obtained from the South Dakota Agricultural Experiment Station and their component parts (stalks and leaves) analyzed to determine if one type was better suited for utilization than the other. No significant differences in composition between the stalks of flint and dent types could be found. The flint type contained a somewhat greater amount of water-soluble material, but this could be attributed to differences in maturity between the two types. A study was made of the published methods for determining xylose, pentosans, and uronic acids when applied to agricultural residues. None of three methods (Breddy and Jones, naphthoresorcinol or orcinol colorimetric, carbon dioxide evolution) was found satisfactory when tested on both standard and purified materials such as xylose, galacturonic acid, glucose, xylan, and pectin, and natural products such as corncobs.

SUNDRY NEW PRODUCTS

Noreseal--A Cork Substitute

Due to short supply of brewers' and soft drink raw materials the field tests on the lot of 70,000 dispensed Noreseal crowns have not yet been completed. However, preliminary tests by five of the leading brewers, a number of soft drink companies, and manufacturers of cork crown seals have been made on this lot. The practical tests made in brewery and in soft drink bottling houses on a total of about 10,000 crowns were uniformly excellent. One of the largest breweries indicated in writing that in certain respects Noreseal was superior to composition cork. The tests made by the crown cork seal manufacturers were all laboratory tests and in some cases were unfavorable. When it was called to the attention of those companies submitting such unfavorable reports that practical tests were uniformly satisfactory, several companies sent in revised reports showing satisfactory performance of Noreseal. It is hoped that limited industrial production will be undertaken in 1947.

Soft-Grit Blasting

Considerable favorable publicity of this method of cleaning metals has resulted in hundreds of inquiries to the Northern Laboratory. Present information indicates rather wide use of this method by the glass and rubber industries for cleaning molds, by the automotive industry for cleaning spare parts, particularly in engine rebuilding, and in foundry practice for cleaning mold cores and boxes. This investigation is being extended to the use of ground nut shells and other agricultural wastes as a source of soft-grit materials.

Shotgun Wads

Cooperative work with a large producer of sporting powders has led to the manufacture of a superior shotgun shell wad from specially prepared wheat straw.

ALCOHOL AND OTHER LIQUID FUELS

Synthetic Liquid Fuels Investigations

The research work under the Synthetic Liquid Fuels project is closely coordinated with that of the Northern Laboratory, which, since its founding, has been engaged on various phases of the problem of fuels from agricultural products.

The purpose of the Synthetic Liquid Fuels Project is to determine the manufacturing steps and costs on a semi-works scale of a process for the hydrolysis of agricultural residues to sugars, in solution of high concentration; and to lignin. The motor fuels testing laboratory is investigating the value of fuels produced from the sugars, from furfural, or from lignin. Investigations on crystallizing xylose or glucose from the sugars, the development of chemical derivatives from the sugars or from furfural, as well as uses for lignin, other than for fuel, are being undertaken by this Laboratory. Progress to date has been quite satisfactory.

Butyl Alcohol Fermentation of Xylose Liquors

It has been found possible to ferment xylose saccharification liquors obtained through the hydrolysis of corncobs to butyl alcohol, acetone, and ethyl alcohol. Of a variety of treatments studied it was found that charcoal treatment materially improved the saccharification liquors for fermentation. If, in addition, reduced iron was added in small amount, good fermentation of the liquors was guaranteed. Reduced iron serves both to reduce the oxygen tension of the medium and also to remove excess copper which is introduced through corrosion of the bronze equipment used in making the hydrolysates.

Fermentation of the hydrolysates could be obtained in many cases without pretreatment with carbon, provided reduced iron was used. Some other commercial preparations of finely divided iron have also been found effective in making the liquors fermentable.

Motor Testing of Synthetic Liquid Fuels

Since from the standpoint of motor testing, the liquid fuels derived from agricultural residues usually are the same as those derived by fermentation of cereal crops comprising such substances as alcohol, furfural, butyl alcohol and acetone, all studies on this subject will be given under the report on "Corn, Wheat, and Other Cereal Crops Utilization Investigations" with the same title of "Alcohol and Other Liquid Fuels."

Publication of a bibliography on "Construction, Design, Economics, Performance, and Theory of Portable and Small Stationary Gas Producers" has aroused more than the expected interest. The Wellman Engineering Company, Cleveland, Ohio, has built a large gas generator, designed for use of agricultural residues as fuel. It is understood that although this unit is to be sold to South American interests, the company is looking for a market in this country also.

PLASTICS, ELASTOMERS, AND RESINS

Noreplast-R (R = Residues)

Some industrial interest has developed in the use of Noreplast containing 25 percent phenolic resins, 50 percent corncob or rice-hull flour, and 22 percent mineral filler. Work in a large molding plant has led to better formulation of this molding powder. The use of fillers made by grinding nut shells is being explored to round out and complete the information on residue fillers for plastics.

Noreplast-L (L = Lignin)

Much work has been directed to the use of saccharification lignin in plastic materials but without much success so far. Efforts to improve the properties of asphalt by compounding with lignin has led to no valuable results. While it has been possible to formulate phenolic plastics using lignin and cresols, the results obtained were erratic. At times molded objects were obtained with excellent strength properties, but results could not be consistently duplicated. Work directed to the use of furfural, furfuryl alcohol, and vinsol resin combinations, with lignin as a filler, are under way. Preliminary results are not outstanding.

SYNTHETIC ORGANIC CHEMICALS AND INTERMEDIATES

Hydrogenation and Dehydrogenation Products from Furfural

A number of samples of 1,2-, 1,4-, and 1,5-pentanediols have been prepared and distributed to industrial companies for use evaluation. One large rubber company reports that preliminary investigations of the use of 1,5-pentanediol shows it is quite satisfactory for the preparation of esters of various molecular weights up to the superpolymer range. Several of these esters form fibers which can readily be drawn to an elongation of 400 percent. This company has undertaken a theoretical investigation of the properties of these esters. γ -Valerolactone is an intermediate useful for producing a variety of chemicals. A yield of 70 percent of theory has been obtained from the dehydrogenation of 1,5-pentanediol. Attempts to produce the amino acid, proline, for which no particularly good synthesis exists, by starting with furoic acid or methylfuran have so far been unsuccessful. The possibility of producing the amino acid, lysine, starting with γ -valerolactone is also under way.

Derivatives Arising from Opening of Furan or Pyran Rings

The synthesis of 4,4'-dichlorobutyl ether has been improved by reacting tetrahydrofuran with POCl_3 and H_2SO_4 to give yields of 65 percent of theory. Attention has been directed to the preparation of derivatives which might prove of industrial interest. For example, the ether is converted to oxydivaleronitrile and hydrolysed to oxydivaleric acid with good yields in both steps. Esters prepared from this acid are high-boiling compounds of possible interest as plasticizers. The dichlorobutyl ether has been converted to the dimethoxy and diethoxy dibutyl ethers which are also high-boiling liquids having good solvent properties and which may find use as plasticizers. Upon hydrolysis the diacetoxymethyl ether is converted to 4,4'-dihydroxymethyl ether which is analogous in structure to diethylene glycol. By reducing oxydivaleronitrile the 5,5'-diaminodimethyl ether is obtained in 85-percent yield. This may be of interest for the production of linear polymers of the nylon type. By carrying on analogous halogenation of tetrahydropyran it has been possible to produce the 5,5'-dichloromethyl ether in about 20-percent yield.

In connection with this development work it is noted that E. I. du Pont de Nemours and Company has announced plans to construct a plant for the production of tetrahydrofuran. The plant will start operations early in 1947. Projected price is 40 cents per pound. The Quaker Oats Company has purchased The Q-O Chemical Company, manufacturers of furfural for the Government, at Memphis, Tennessee. Estimated present production capacity for furfural is 20,000 tons per year. Corn cobs are used chiefly as raw material at an annual rate of about 150,000 tons.

CHEMICALS DERIVED FROM FERMENTATION

Pentonic Acids

The oxidation of xylose, as well as arabinose, to the corresponding pentonic acids by application of species of Pseudomonas has been studied. It was found that a number of these species were capable of oxidizing the pentoses with best yields from the corresponding pentoses of about 25 percent of d-arabonic acid, 50 percent of l-arabonic acid, 72 percent of d-xylonic acid, and 77 percent of d-ribonic acid.

CELLULOSE PULPS FOR PAPER AND BOARD MANUFACTURE

9-Point Corrugating Strawboard

It was hoped that the improved process for producing strawboard could be tried out on a mill scale, but the company desirous of making this trial has been unable so far to obtain the necessary refining engine. The test is still planned, however. Neutral sodium sulfite has become available in large tonnage. The Northern Laboratory has been working with the supplier of this chemical and with several board companies to determine if this chemical can replace lime and caustic as

a cooking agent. The results at present are very promising. Excellent progress has also been made on the development of a moisture meter to determine the moisture content of baled straw, a subject of great interest to the strawboard industry.

Fine Paper Pulps from Straw

With the increasing cost and shortage of pulp wood and with the great expansion in the paper industry, some improvement in the economics of straw pulping should open the door for use of straw in the manufacture of fine or specialty papers. A detailed experimental examination of the more important pulping methods has led to intensive investigation of the neutral sodium sulfite method to pulp straw. Yields of bleached screened pulp of 50 percent of the dry straw are being obtained. Sometime ago when Dutch paper-mill engineers visited the Northern Laboratory, it was suggested they try out this method. Advice from them now indicates that one mill, following 3 months of study, is producing 100 tons of excellent pulp per week by this procedure. An American mill is anxious to try this process for the production of liner for a specialty board. Work has almost been completed with paper engineers from China and from the Philippines on the pulping of rice straw. Taking into account the chemicals available in the Orient, the kraft cooking process appears most applicable.

BUILDING AND CONSTRUCTION MATERIALS

Insulation and Hardboard Fundamental Fiber Studies

The fundamental studies on fiber relationships in insulation and panel board manufacture are proceeding in a most satisfactory manner. From this study a series of practical results have been obtained, so that the Northern Laboratory is now prepared to give information on the use of straw for the large-scale manufacture of a series of building board products to companies or individuals capable of commercializing this information. One company has been furnished manufacturing details for the production of low density products suitable for asphalt saturation and use as expansion joints, traffic board, etc. Two groups in Kansas and one in Nebraska have expressed the desire to enter building material manufacture, and this Laboratory is working closely with these people. If these plans carry through, use for about 200,000 tons of straw per year will follow.

The wire-bound box industry uses about 1-1/2 billion square feet of low-grade veneer per year. This is made, for the most part, in small mills in the South. The forests there are being depleted and the veneer is finding use in higher-priced markets. This situation is causing extended research investigations of substitute products for the wire-bound box industry. Tests on 10 boxes made from a special panel board produced at the Northern Laboratory from wheat straw have given results, which, while not satisfactory, are still of considerable promise. Improvements of the panel board to overcome its deficiencies appear possible. If the veneer use were converted to straw panel board, about 1 million tons of straw would find a new outlet market.

CORN, WHEAT, AND OTHER CEREAL CROPS UTILIZATION INVESTIGATIONS

COMPOSITION AS AFFECTED BY VARIETY, BREEDING, ENVIRONMENT, AND MATURITY

Studies on Development of Starch Granules

Studies were continued on starch from dent, glutinous, and sweet varieties of corn at different stages of maturity. The bound water of starch granules at 12 to 13 days after pollination was 0.8 to 1.0 gram per gram of starch. The amount of bound water decreased with increase in maturity. Differences among starches from the three varieties were not significant. The so-called dextrin globules of sweet corn showed some of the properties of coacervates as defined by Bungenberg de Jong. This is of interest in our theory previously advanced that starch granules may be formed in the plant by coacervation of the polymerized carbohydrate.

Oil Content of Corn as Influenced by Heredity

Previous work has shown that the oil content of hybrid corn, grown on the majority of Corn Belt farms, is influenced largely by the pure inbred-lines used to produce the hybrid seed. Attention has been concentrated on oil content because the price per pound of oil is higher than any other major constituent of corn and because corn oil represents a major source of income for the wet- and dry-corn millers and some representatives of the fermentation industry. Many additional analyses have been completed on single crosses of various inbred lines in order to find those inbred lines best suited for high-oil hybrids. Sufficient data have been obtained to make it probable that analysis of the parent inbred line will be sufficient to assess its performance in the final double-cross hybrid.

COMPOSITION AS AFFECTED BY RAW MATERIAL PROCESSING AND STORAGE

Oil in Components of the Corn Kernel

Eleven samples of corn of widely varying types have been carefully hand dissected and the components (endosperm, germ, and bran) analyzed. That portion of the oil in corn which may be recovered commercially is in the germ, and the results of these analyses show that the oil in the germ is proportional to the total oil in corn of both high and low oil content.

ALCOHOL AND OTHER LIQUID FUELS

Motor Tests

To evaluate new motor fuels properly, studies must be made on many physical properties such as density and vapor pressure, not only for the mixed fuel but also for the pure components. Other factors such as gum stability and corrosiveness must be measured. After a full program of

such laboratory studies, the final test of motor fuels is given by road tests. Many blends of alcohol with gasoline have been studied by use of the single-cylinder test engine and, for a full-scale dynamometer test, by use of a 1941 Plymouth engine. Fuels studied included two standard gasolines with amounts of alcohol from 10 to 50 percent pure alcohol, and blends containing benzene. Many factors such as specific fuel consumption, efficiency, brake horsepower, etc. were evaluated for all of these fuels.

As a brief and incomplete summary of this work it may be stated that best performance for high-alcohol blends requires higher compression ratios than 7.3; with standard carburetor jets 25 percent alcohol gives highest efficiency but pure alcohol the most power; engine roughness occurs only for blends with over 50 percent alcohol and may be reduced by manifold heating (with some power loss); for pure alcohol, fuel injection seems preferable.

In continuation of previous studies of ethanol-hydrocarbon systems, the density of ethanol and the thermal expansion and vapor pressure of the ethanol-isooctane system have been measured with great precision. Preliminary studies on the kinetics of combustion have been made and analytical methods surveyed for use on this problem.

Work has been essentially completed on a very complete summary of published work on alcohol as a motor fuel. This will appear as a Department of Agriculture publication.

Fungal Enzymes

It has been demonstrated that a number of species of Aspergillus are capable of producing high levels of α -amylase when they are cultured by deep-vat procedures. These filtrates may be used to saccharify grain mashes with the production of high alcohol yields. It was noted that good alcohol yields depended not only upon α -amylase production, but also upon the maltase activity of the filtrates. Species of Aspergillus (for example, Aspergillus niger NRRL 679) which produce high levels of maltase activity as well as α -amylase activity, resulted in more rapid alcoholic fermentations when filtrates of their cultures were used as saccharifying agents. Fungal amylase systems containing good maltase activity rapidly converted starch, dextrans, and maltose to glucose, whereas malt degraded starch to dextrans and maltose and then only slowly to glucose.

Crude filtrates of a number of mold cultures have been investigated for ability to hydrolyze various polysaccharides. In general it was found that all mold filtrates studied were capable of hydrolyzing maltose, inulin, sucrose, and the α -limit dextrin obtained from potato amylopectin. None of the mold filtrates studied were capable of hydrolyzing lactose, α -methyl-d-glucoside, levoglucosan, calcium lactobionate, and calcium maltobionate.

Five of the most promising strains of Aspergillus niger studied in the laboratory have been tested in the pilot plant for use in the production of alcohol. Experiments have been conducted in which the fungi were grown by submerged fermentation on thin slop fortified with 1 percent ground corn and 0.5 percent calcium carbonate. The enzymatic liquor produced was used to saccharify 1,200-gallon batches of grain mashes and the converted mashes were fermented with yeast in the usual way. The amount of liquor used was such that it constituted 10 percent of the mash that was fermented.

Two strains, namely, Aspergillus niger NRRL 330 and NRRL 337 were used in series of experiments in which each fungus was grown in thin stillage obtained from the fermentations where it had been used as the saccharifying agent. These particular fungi have been utilized through five cycles with no diminution in the yields of alcohol. On the average, the yields of alcohol amounted to 5.1 proof gallons per bushel of grain fermented.

FIBERS, FILMS, PROTECTIVE COATINGS, AND ADHESIVES

Fibers from Zein

Construction of equipment for the continuous wet spinning of zein fibers has been completed. It has been demonstrated that a mild formaldehyde treatment after the coagulating bath is necessary for the preparation of good fibers. Acetylation of the fiber prior to the final formaldehyde cure has been studied extensively. It was found that proper acetylation increased the resistance of the fiber to boiling water, decreased the dye uptake, moderated the effect of the final formaldehyde cure, and assisted in removal of pigments. The acetylation was carried out in acetic anhydride under a wide variety of conditions. Sodium acetate and sulfuric acid were effective catalysts. Acetyl content in excess of 5 percent was easily obtained in a short time in continuous processing equipment. There is a strong commercial interest in the fiber. Two commercial firms have modeled their experimental equipment and procedure after that developed at this Laboratory.

Plywood Adhesives

The success attained in extending phenolic resin plywood glue with soybean meal and corn gluten led to similar studies on resorcinol resin glue. Resorcinol and formaldehyde make a weatherproof resin glue which cures at normal room temperature. This is very important in the fabrication of laminated beams, airplanes, boat keels, and odd-shaped pieces which cannot be handled satisfactorily between the flat platens of a hot press. Preliminary experiments showed that corn gluten was more adaptable as an extender for the resorcinol resin than soybean meal. No further tests have been made, therefore, with the soy meal.

Amylose Triacetate Fibers

Amylose fibers have been prepared by deacetylation of amylose triacetate fibers in alkaline anhydrous ethyl alcohol. The fibers are lustrous and pliable. Microscopically they are indistinguishable from the acetate fibers. Their tensile strength is from 0.2 to 0.3 grams per denier. The strength of amylose triacetate fibers after a suitable stretching treatment has been raised from 0.5-0.6 to 1.5 grams per denier. These laboratory stretching experiments will require verification in larger-scale operations before their practicability can be determined.

Measuring Orientation in Fibers, Films

X-ray pictures have been made of amylose acetate, propionate, and butyrate films and fibers and of amylose films and fibers after deacetylating. Since the X-ray fiber pictures offer the most convenient method of measuring orientation, a very extensive series of such pictures have been made after various physical treatments of the films and fibers. Similar pictures have been made of relaxed fibers, and measurements of density were also made of both stretched and relaxed fibers. These data are useful in combination with physical tests, such as for tensile strength, to obtain the best and most useful properties.

SYNTHETIC ORGANIC CHEMICALS AND INTERMEDIATES

Formaldehyde Derivatives of Dextrose

Further knowledge of the chemistry of 2,4;3,5-dimethylene-D-gluconic acid has been obtained. A new compound, methyl 2,4;5,6-dimethylene-D-gluconate has been obtained in 22-percent yield by heating the methyl 2,4;3,5- compound in vacuo. The 2,4-methylene derivative was also isolated and identified. The allyl ether ester of dimethylene gluconic acid after polymerization with sodium peroxide produced a product that merits further study as a coating material.

Starch Esters

Methods have been developed for the controlled synthesis of mixed esters of amylose. Working quantities of a number of mixed esters have been prepared and their solubility and molding characteristics determined. Replacement of but 0.4 of one acetyl by a propionyl or butyryl radical is sufficient to solubilize amylose acetate in acetone. This property allows acetone to be used as a solvent instead of chloroform in the preparation of solutions used in fiber making.

Interesting new compounds have been obtained by reacting starch, amylose, and amylopectin with phenyl isocyanate in pyridine solution at 100° C. for 6 to 8 hours. Non-pretreated starch granules reacted completely. Pretreatment of the granules was required when fatty acid anhydrides were used in making starch esters. In contrast to all starch

esters previously prepared, the tricarbanilates are levorotatory in pyridine. The carbanilates have unusual solubilities, optical rotations, and stabilities which indicate utility in both theoretical and practical applications.

Oxystarch

Periodate oxystarch has been oxidized with bromine and then hydrolyzed with acid to give D-erythronic acid in 85-percent yield. This is almost three times the yield obtained by the bromine oxidation of hydrolyzed oxystarch. This improvement is important in the development of an economical process for producing D-erythronic acid.

NEW AND IMPROVED FOOD AND FEED PRODUCTS

Microbiological Vitamin Synthesis

Experiments on the development of economical media for the production of riboflavin by *Ashbya gossypii* have been continued. Certain byproducts of the meat packing industry, notably, tankage and beef stick liquor, have been capable of substitution for peptone. Using these ingredients, yields of 400 to 500 micrograms of riboflavin per ml. are regularly obtained after a 5-day fermentation period.

Vitamin Content of Cereal Grains

Studies of the vitamin content of a large selection of grain sorghums indicated that nicotinic acid levels may be markedly influenced by the variety employed in producing the hybrid. To examine this possibility further, a series of 339 samples of heads from different plants of the Westland-by-Cody cross, obtained through the cooperation of the Fort Hays branch of the Kansas Agricultural Experiment Station, was analyzed for nicotinic acid. Westland contained about 42 micrograms of nicotinic acid per gram and Cody about 71 micrograms per gram. Of the series of samples of the progeny that were analyzed only 3 percent contained the vitamin in a concentration equal to or lower than that found in the Westland parent, whereas 23 percent contained the vitamin in concentrations equal to or greater than those found in the Cody parent. Three samples contained more than 100 micrograms of nicotinic acid per gram.

Survey studies have been extended to oats, rye, barley, and wheat. No evidence has been obtained to demonstrate that marked differences in vitamin content are related to variety.

EXTRACTION, RECOVERY, AND PROPERTIES OF SPECIFIC CARBOHYDRATES, OILS, AND PROTEINS

Wet Milling of Damaged Corn

The prevalence of quantities of soft corn in recent crop years has made it necessary to examine the milling characteristics of moldy and heat-damaged corn. Increasing the SO₂ content of the steep liquor or prolonging the steeping time resulted in better operation and yields. Badly molded or heated corn produced but one-half as much starch as sound corn.

Wet Milling of Artificially Dried Corn

Samples of artificially dried corn have been processed for starch on a laboratory scale. The results cannot be accepted as conclusive owing to difficulties encountered in the control of variables during drying. Indications are that excessive exposure to heat causes changes in the protein, making the separation of starch difficult. Tentatively corn destined for use by wet-process millers should not be dried to a moisture content lower than 11 percent and the relative humidity during drying should not drop below 10 percent.

Effect of Various Steeping Agents on Corn Wet Milling Operations

Most corn wet-process millers are anxious to process more corn at present, but plant capacity is usually limited by the number of steeping tanks installed. If the steeping period, which is usually 36 to 40 hours, could be shortened, the capacities of plants so handicapped could be increased substantially. Experiments have been conducted for testing possible steeping and wetting agents which might be used to speed up the steeping operation. Of several substances tested, none has been found which is as efficient as sulfur dioxide.

Production of High Quality Glucose Sirup from Wheat Flour

During the past 3 years many industrial concerns have displayed considerable interest in the Batter Process which was developed at this Laboratory. Several companies have adopted it on a commercial scale primarily for producing a sirup and dextrose from the starch slurry. The sirup produced by hydrolyzing the starch milk directly is brown in color and possesses what, for certain purposes, is an objectionable taste. The objectionable taste and color are caused by a relatively large amount of protein in the starch milk.

Experiments for removing the bulk of the protein from the starch prior to its conversion to glucose have been conducted in order to obtain a finished product which more nearly approaches corn glucose sirup. The method under investigation consists in allowing the starch milk to settle for approximately 16 hours at room temperature after which the supernatant liquor is decanted and fresh, softened water is added to bring the slurry back to its original volume. The resulting liquor can be filtered through a plate-and-frame filter press with rates as high as 2.4 gallons per sq. ft. per hour. The filter cake is blown with air while it is still in the press and this frees the starch of most of the dissolved protein. The starch is removed from the filter press and processed in practically the same manner as that used in the conversion of corn starch to glucose sirup. The conversion can be carried out either under pressure or in open converters similar to those now being used in the plants utilizing the Batter Process. The finished sirup is clear and almost water-white; it is quite sweet and possesses very little salty or after-taste; it is comparable to the highest grade of corn sirup on the market.

Microscopic Studies of Barley Endosperm

The project for determination of the structural characteristics and the chemical and physical relationships in seeds of cereal grains is being continued. As with corn, the first grain studied, the starch granules of barley endosperm have been shown to lie embedded in a proteinaceous matrix. A method was developed for the removal of starch that left the three-dimensional network of protein material intact. This network in barley endosperm is much weaker than the corresponding network in corn. Studies will be continued to include wheat and other cereals.

Comparative Studies on Starches from Widely Different Sources

Starches from large numbers and varieties of plant seeds, roots, tubers, and rhizomes are being characterized and fractionated. The discovery of varieties having unusual properties and amylose content would be of scientific and practical value. Aside from the starch of wrinkle-seeded garden-type peas which contains 60 to 70 percent amylose, the starches highest in amylose are those of field peas, vetch, and several varieties of beans which contain from 32 to 35 percent amylose. No correlation has been found between amylose content and the site of starch deposition within the plant.

Pasting Characteristics of Starches

Light-transmittancy values have been obtained during the pasting of 0.1 percent suspensions of starch from dent corn, waxy dent corn, potato, iris, canna, acorn, horsechestnut, sorghum, rice, buckwheat, mung bean, and field pea. No correlation was found between the form of the curve and the source of the starch. Below the gelatinization temperature the translucency of the suspension is closely related to the average granule size. There is evidence that determinations of light transmittancy of starch pastes should be made on the basis of equal numbers of granules instead of equal weight concentrations in comparing different starches.

Properties of Specific Carbohydrates

Measurements of water sorption have been made on starches from various sources as well as on amylose and amylopectin. The work of others has shown that the energy of water sorption is nearly the same for adsorption or desorption and amounts to about 12.1 Kcal/mole for all starches. The capacity of starches to absorb water has shown a correlation with the intensity of the rings found in X-ray patterns in work at this laboratory. Two types of patterns A and B are observed in many starches and the relative intensities of these patterns is related to the water sorptive power of the starch. The densities of some of these starches at various degrees of hydration have been measured and the changes in density together with changes in linear dimension enable calculations of pore spaces in the starch granules to be made.

STRUCTURE AND OTHER BASIC INVESTIGATIONS

Degradation of Amylose by α -Amylase

The hydrolysis of starch by the α -amylase of barley malt is of importance in fermentation industries as well as in studies of starch structure. The action of α -amylase on potato amylose (used because it retrogrades slowly) produced, predominantly, low molecular weight polysaccharides and dextrans. Fractionation of the hydrolysate by alcohol precipitation resulted in a major fraction which appears to be a dextrin of about six glucose units. Methods are being sought for the isolation of a dextrin of definite molecular weight in pure form.

6- α -Glucosido-Glucose

The presence of α -1,6-linkages in starch is believed to be involved in the incomplete hydrolysis of starch by acids and enzymes. To obtain information on the behavior of α -1,6-linkages, studies were carried out on the bacterial polysaccharide dextran formed by Leuconostoc mesenteroides. We have been able to grow this organism to give dextran with a relative viscosity of 2.00 to 2.23 in 24- to 27-percent yield. Acid hydrolysis of the dextran was 95 percent complete in 72 hours, whereas under the same conditions hydrolysis of waxy cornstarch was 97 percent complete in 25 hours. The critical increment between 80° and 90° C. with 1 N sulfuric acid was 3,300 cal. per mole greater for dextran than for the waxy cornstarch and the temperature coefficient was 4.0 and 3.5, respectively. Thus, the α -1,6-bond is hydrolyzed more slowly than the α -1,4-bond. Also the difference in rates of hydrolysis of these two polysaccharides is greater at the lower temperatures.

CHEMICALS DERIVED FROM FERMENTATION

Antibiotics

Survey studies on the microorganisms contained in the Culture Collection, as well as on new isolates, are being conducted with the object of developing new antibiotics. As a result of the surveys so far completed, about 60 antagonists have been found which show various antibiotic spectra against the following test organisms: Brucella abortus, Brucella bronchiseptica, Escherichia coli, Staphylococcus aureus, and Mycobacterium smegmatis. It is planned to carry the more promising antibiotics through the necessary developmental stages to obtain therapeutically useful preparations. This development will be carried forward in cooperation with the National Institute of Health.

α -Ketoglutaric Acid

A new fermentation process resulting in the production of α -ketoglutaric acid has been discovered. This chemical is produced by the fermentation effected by Pseudomonas fluorescens by allowing the process to proceed to the point at which the ketogluconic acid is dissipated. Yields of α -ketoglutaric acid as high as 25 percent have been obtained.

Production of Citric Acid in Submerged Culture

The production of citric acid by submerged culture methods, rather than by the surface methods now employed industrially, would represent a distinct technical advance. Extensive study of this fermentation has resulted in citric acid yields by the submerged process that compare quite favorably with those obtained by surface methods.

Bionic Acids

It has been found that a strain of *Pseudomonas graveolens* (NRRL B-14) will oxidize the disaccharides, maltose and lactose, to the corresponding bionic acids. The yields obtained are 80.2 grams of maltobionic acid from 100 grams of maltose and 77 grams of lactobionic acid from 100 grams of lactose. These results are of special interest in that they demonstrate for the first time the direct metabolism of disaccharides by bacteria without prior hydrolysis. The fermentation process has the advantage of simplicity over chemical processes which may be applied for the production of the same acids.

Culture Collection

In addition to many other activities, the Culture Collection Section is conducting taxonomic studies on the genus *Penicillium* which are jointly sponsored and supported by the Department of Agriculture and the National Science Fund. Comparative examination of cultures belonging to almost all of the major groups within the genus have been made, and from the resulting study a briefer and more useful taxonomy is being developed. The results of this work will be published in a book, "A Manual of the *Penicillia*," which is in the course of preparation.

SOYBEANS AND OTHER OILSEED CROPS UTILIZATION INVESTIGATIONS

COMPOSITION AS AFFECTED BY VARIETY, BREEDING, ENVIRONMENT, AND MATURITY

Oilseed Composition

In cooperation with the Illinois Agricultural Experiment Station, analyses on an extensive series of sunflower and safflower samples have been made for two successive years. These analyses are needed to find the proper varieties, time of planting, and rate of seeding, if these oilseeds are to be grown successfully for industrial use.

Oil Composition

Uses for vegetable oil depend on the kinds and amounts of fatty acids present as triglycerides. While there are published methods of analysis for these acids, these methods are excessively difficult, time-consuming, and of doubtful accuracy. The methods have been studied a great deal but agreement among laboratories has been poor; no general knowledge of the causes of error nor of the extent of overall accuracy is available.

Recently alkali conjugation of the oils, followed by spectrophotometric determination of the conjugated arachidonic, linolenic, and linoleic acids has been proposed. Our studies have shown that this method does not give results in agreement with older methods, that the older methods are not in agreement with each other, and that for both methods the directions do not give information sufficient to control all the important variables. Extensive studies on both oils and purified methyl esters of fatty acids have been made. In the alkali conjugation the effects of time, temperature, concentration of alkali, and other factors have been evaluated. In the thiocyanogen determination the effect of several factors, such as moisture and certain impurities, has been shown to be unimportant within certain limits.

COMPOSITION AS AFFECTED BY RAW MATERIAL PROCESSING AND STORAGE

Changes in Oil Content of Soybeans

For two successive seasons, freshly harvested soybeans have been stored under commercial conditions and the oil content, as determined by analysis, measured over a period of several months. In neither season has the oil content changed on storage. This should answer the common rumor among processors that there is a decrease in oil content on storage.

FIBERS, FILMS, PROTECTIVE COATINGS, AND ADHESIVES

Catalytic Isomerization of Non-Conjugated Fat Acids and Their Derivatives

As a part of the program to find replacements for tung and oiticica oils, the study of isomerization catalysts has been continued. In addition to the nickel-carbon catalyst which has been reported previously, new catalysts have been found which cause methyl linoleate, methyl esters of soybean fat acids, soybean oil, linseed oil, and similar materials to develop substantial amounts of conjugation. Unlike the products obtained by alkali conjugation or conjugation with the nickel-carbon catalyst, the new oils contain significant amounts of triene and tetraene conjugation. A typical specimen of soybean oil isomerized with the new catalysts contained 12.5 percent diene conjugation, 6.3 percent triene conjugation, and 1.1 percent tetraene conjugation; total, 19.9 percent conjugation.

By heating the catalytically treated oils to 150°-250° C. in vacuo, increased amounts of triene and tetraene conjugation can be obtained. A typical oil contained 10.7 percent diene conjugation, 16.1 percent triene conjugation, and 5.3 percent tetraene conjugation; total, 32.1 percent conjugation.

Because tung and oiticica oils owe their desirable properties to the high percentage of fat acid components containing triene conjugation, the properties of the thermally treated oils should resemble those of tung and oiticica oils to a greater degree than do those of previously available synthetic conjugated oils. Preliminary evaluation has shown that the thermally treated oils without addition of metallic driers, dry

in 1 hour or less to frosted or wrinkled films which do not develop after-tack. The color of the films is water-white, despite the rather dark color of the original oil. Attempts to formulate varnishes have been hindered by a tendency of the oils to crack at 300° C. with liberation of undesirable decomposition products; however, it should be possible to process these highly reactive oils at lower temperatures. In paints, rapid drying and the bleaching effect are retained in the presence of titanium dioxide. Other pigments have not been examined.

Preliminary cost estimates were made for the production of conjugated soybean oil by the catalytic (nickel-carbon) isomerization process. The design calculations were based on a plant producing approximately 60,000 pounds of the finished product per day. Two methods of operation were selected, one in which the spent catalyst is discarded and the other in which the nickel of the catalyst is recovered. For the former method the processing cost would be 0.78 cent per pound of product and for the latter this figure would be reduced to 0.55 cents. The cost of the raw material, administration, and selling were not included. The capital investment for the plant would be approximately \$65,000 in each case.

Improved Soybean Oil Paint Coatings by the Addition of Lime

The addition of lime (calcium oxide), in amounts of 5 to 10 percent by weight, to the pigment contents of outside white paints has improved the coatings of paints containing all or large amounts of soybean oil in the following respects:

1. The coatings are free from both residual and after-tack. The former is the sticky feel still present on the coating after being air dried for several days, while the latter is the softening and consequent stickiness of the coating usually caused by exposure to the heat of the sun. Both of these conditions are typical of the coatings from paints containing large percentages of soybean oil, and lead to excessive dirt pickup and retention that cause the coatings to become unsightly and gray. With 5 percent of lime in the pigment, even 100 percent soybean oil paint coatings do not collect or retain dirt. The coatings have remained clean and white when exposed to outdoor weathering for more than a year at an angle of 45° facing south.
2. The coatings do not turn yellow when screened from the bleaching effects of the sun as do linseed and untreated soybean oil paints containing no lime.
3. The durability of coatings from similar paints containing lime has been improved over those without lime in all of our experimental weathering tests, especially when a conjugated soybean oil, treated by the nickel-carbon method, was used as the sole drying oil. Film erosion that results from chalking has been considerably decreased; also, checking and cracking have been retarded for longer periods because of the added lime.

Soybean Protein - Isolation and Use in Paper Coatings

A "short cut" procedure for the isolation of soybean protein has been devised, and found suitable for use at the site where the protein is to be used. The protein isolated by the new modification has a purity of 30 to 35 percent and appears to be satisfactory for those adhesives needed in paper coatings, shotgun shell casings, and probably other products.

In this modified process the centrifuging is eliminated. Hot precipitation of the protein hastens formation of large curd particles that can be readily separated on a wire screen rather than by a filter. The use of the wet curd in place of the dry protein eliminates the drier. Thus the cost of three pieces of expensive equipment (centrifuge, filter, and drier) and their operation is eliminated. Manufacturing costs of producing suitable protein for many adhesive purposes, therefore, is substantially reduced. Protein prepared by the "short cut" method for trial runs in a paper coating mill has given highly satisfactory results.

Shotgun Shell Casings

The use of soybean protein as an adhesive in the manufacture of shotgun shell casings has given very good results. Shotgun shell casings are made by rolling a special sheet of paper on a mandrel while spreading a thin solution of glue over the surface of the paper. The cylindrical laminated casings are discharged from the machine at the rate of 50 to 60 per minute.

Because of the unavailability of casein, the manufacturer tested a wide variety of synthetic adhesives, none of which was satisfactory. At the request of the manufacturer this Laboratory developed a formula based on soybean protein, and which was found to be somewhat superior to the formula utilizing casein. In particular, the shell casings were "tougher" or more "leathery" and had better "water resistance," both characteristics being improvements in the right direction.

NEW AND IMPROVED FEED OR FOOD PRODUCTS

Flavor Stability of Soybean Oil

Progress on the critical flavor stability problem of soybean oil was accelerated by an investigation of the German Oil Processing and Refining Industry conducted by a member of our staff who was loaned to the Technical Industrial Intelligence Committee. The investigation revealed certain methods of refining soybean oil that reportedly improve flavor stability. One method involves a particularly thorough degumming operation and the subsequent addition of a small amount of citric acid during deodorization. This process has been tested on a laboratory scale and more recently on full commercial plant scale. It has been found to have considerable merit; that is, the storage life or flavor stability of the oil is significantly improved.

Concurrently with this work, we have developed and applied systematic procedures to the refining and organoleptic testing of soybean oil that permit us to evaluate the effect of any variation in any processing step upon flavor stability.

Nitrogen in Oil

In studying the mysterious phenomenon of "reversion" in soybean oil it has been felt that nitrogen bodies in the oil may be responsible. The limits of nitrogen which could be determined in oil have been too high to investigate this point satisfactorily. A method for determining nitrogen in oil has been devised which, by means of a preliminary acid extraction, permits the use of oil samples up to several hundred grams. In highly refined edible soybean oil 0.0002 percent nitrogen was found.

EXTRACTION, RECOVERY, AND PROPERTIES OF SPECIFIC CARBOHYDRATES, OILS, AND PROTEINS

Fractionation of Soybean Oil by Liquid-liquid Extraction

During previous work it was noted that the addition of naphtha to the furfural entering the extraction column increased the stability of the fractionation operation in that its presence decreased flooding. Earlier tests had indicated that the degree of separation obtained was affected by the amount of naphtha used. Accordingly, a series of pilot-plant experiments has been carried out with the object of determining the proper amount of naphtha required.

The tests indicate that the use of about 50 percent of the theoretical amount of naphtha gives the best results. With this proportion of solvent the equipment operates more smoothly and a higher temperature may be employed which increases the solubility of the oil in the selective solvent.

Further studies have been made on the effect of maintaining the interface in various parts of the extraction column. About 47 tests were made in which the interface was held near the bottom of the extraction tower. Previously, the equipment had been operated with the interface either at the top or at the midpoint of the apparatus. The results indicate that, in general, the best extraction is produced when a large portion of the extraction tower is filled with the raffinate layer; that is, when the interface is either at the midpoint or near the bottom.

By use of improved equipment and under optimum conditions, as determined to date, results obtained with the 18-foot extraction column are equal to those obtained in the past with a 54-foot extraction column. Furthermore, the fact that a better raffinate oil is produced by lengthening that section of the column which is devoted to the stripping action demonstrates the flexibility of the process and enhances its possibility of commercial adaptation.

AGRICULTURAL CHEMICAL RESEARCH DIVISION

L. F. Martin, Head

Work of the Agricultural Chemical Research Division is in three principal fields: fruit and vegetable processing, primarily on citrus fruits and brined and pickled products; utilization of sugar crops including sugarcane, sugar beets, and sorgo; and production of oil and byproducts from tung nuts. As part of the sugar investigations, research on utilization of a wide variety of agricultural products in candy is carried out in cooperation with the National Confectioners' Association. Approximately three-fourths of the work of the division is conducted at nine field stations, but administrative headquarters and three research sections are housed in the Southern Regional Research Laboratory building. There is research in progress at New Orleans on some phases of all of the projects except those on tung nuts. Field stations engaged in work on citrus fruits are located at Winter Haven, Florida, and Weslaco, Texas, and on brining of cucumber and other vegetable products at Raleigh, North Carolina; work on sugarcane and sorgo is conducted at Baton Rouge and Houma, Louisiana, and at Auburn, Alabama, and seasonally at Meridian, Mississippi; work on sugar beets is carried out during the season in the beet producing areas and at other times at New Orleans; and tung nut investigations are in progress at Bogalusa, Louisiana, and Gainesville, Florida.

SOUTHERN FRUITS AND FRUIT BYPRODUCTS INVESTIGATIONS

Citrus Flavor Essence Recovery

Because of the large and increasing production of citrus fruits throughout Florida and in the Rio Grande Valley of Texas all of the work under this project is currently devoted to problems in the processing of these fruits, and the utilization of byproducts and wastes of processing operations. One problem which has been studied at the Winter Haven Laboratory is the applicability to citrus juices of the method developed by the Eastern Regional Research Laboratory for recovering highly concentrated natural flavor essences. Following preliminary tests employing the Eastern Laboratory's pilot plant, modified equipment adapted to treatment of citrus juices was installed. In addition to the concentrated aqueous essence corresponding to that obtained from apple and other fruit juices, an oil fraction which is insoluble in the aqueous essence is separated from citrus. Rapid flash distillation permits separation of the oil and essence fractions with retention of their characteristic natural flavor and bouquet. By careful control of operating conditions it has been possible to obtain juice stripped of volatile flavor constituents and free of any undesirable flavor. This stripped juice can be concentrated separately under high vacuum and the oil and essence concentrate reincorporated to prepare an orange juice concentrate

which, on reconstitution, compares favorably with the best products of this type yet developed. The process can also be operated to effect simultaneous pasteurizing and de-oiling. Similar equipment has been installed at the Weslaco Laboratory where experiments on the application of this process to grapefruit juice will be investigated during the remainder of the current season.

Production of Feed Yeast

Research on the utilization of citrus byproducts has been concentrated upon the problem of growing feed yeast (*Torula utilis*) from the large volume of waste liquor discharged by citrus pulp feed plants. The investigation is in the stage of practical development on a large pilot plant scale. Under a cooperative agreement with a large canner in Florida the complete pilot plant has been installed adjacent to the feed mill and operated continuously 24 hrs. per day for periods of as long as 12 days. Problems remaining to be solved are primarily of an engineering nature and include determination of the optimum amounts of nutrients and volume of air required, and costs of operation on a large scale. The waste liquor pressed from feed pulp contains from 4% to 6% of fermentable carbohydrates and a cannery discharging 35,000 gallons per day is wasting approximately 15,000 pounds per day of carbohydrate from which over 5,000 pounds of dry yeast can be produced. The feed now manufactured from citrus pulp is primarily carbohydrate and contains only 6% protein; by addition of the yeast which can be produced from accompanying waste liquor, not only can the total feed production be increased but its protein content can be raised to 12%. Of equal importance is the fact that disposal of large volumes of waste containing fermentable sugars is a troublesome and costly problem, and accurate information is being obtained in the pilot plant experiments on the amelioration of this disposal problem. After treatment in yeast production, the resulting effluent contains less than 0.5% fermentable sugars, and the biological oxygen demand is materially reduced.

Histological and Chemical Studies

Survey of the literature reveals that only the more obvious constituent of citrus fruits have been isolated and identified. The nature of many minor constituents is unknown or has only been surmised. There are numerous classes of constituents such as fatty or non-volatile oils and lipids, pigments, phosphatides, etc., which are present in very small amounts, but which may play a role far out of proportion to their concentration in affecting the flavor and keeping quality of canned juices and other products. In order that progress may be made in the practical improvement of the canning process, it is essential that the nature and chemical behavior of these substances be determined and attention has been concentrated during the past year on lipid constituents of var-

ious citrus fruits. This work has been in progress at New Orleans where both histological and chemical investigations have been carried out. Interesting and highly suggestive results of a fundamental nature have been obtained. Peripheral deposits localized in vesicles or juice sacs of the fruits were shown to consist of suberized tissue. By means of electrodialysis the plastid deposits of tissue cells have been collected in quantity and separated into two fractions, the wall structure and internal constituents. From these fractions phosphatide and fatty constituents have been separated as well as certain plastid pigments. Results obtained thus far indicate a significant difference in chemical constitution between phosphatides isolated from the orange and the grapefruit.

Microbiological Studies

Microbiological investigations have been directed toward the collection of cultures in canning plant surveys by the Winter Haven Laboratory, and separation and identification of organisms carried out by the Microbiology Section at New Orleans. Possible effects of specific, non-pathogenic, organisms in contributing to deterioration of canned juices are being studied. Results of fundamental research, both chemical and microbiological, will be applied to practical development of improved processing practices and methods. Both the Winter Haven and Weslaco Laboratories are equipped for pilot scale canning under controlled conditions of experimental packs, and for conducting storage tests on the products.

SOUTHERN VEGETABLES AND VEGETABLE BYPRODUCTS INVESTIGATIONS

Microbiological and Chemical Studies on Cucumber Pickles

Research is conducted at the Raleigh, N. C., Station in cooperation with North Carolina State College on the preservation of cucumbers and other vegetables by salting, brining, and pickling. Attention during the past year has been given to commercial brining tests of new cucumber varieties suitable for Southern growing conditions. Bacteriological and chemical work has been done on the course of both laboratory and commercial brine fermentations and progress is being made on the causes of gaseous fermentation and the formation of "bloaters" or hollow cucumbers. Such cucumbers must be culled from the salt stock and cause serious losses to the industry. Conditions favoring the development of the most desirable bacteria for producing properly brine fermented stock have been determined. More recently a thorough study and identification of yeasts and obligate halophiles isolated from brines has been undertaken, as such organisms are responsible for vigorous gaseous fermentation. Methods will be developed for the control of undesirable organisms. Recommendations have been published on pickle plant sanita-

tion, and standard systematic methods have been prescribed for bacteriological examination of brined, salted, and pickled products including new pasteurized pickle and relish types.

BEET AND CANE SUGARS AND BYPRODUCTS CHEMICAL AND TECHNOLOGICAL INVESTIGATIONS

Aconitic Acid

The outstanding development of the past year in the recovery of valuable byproducts of sugarcane processing has been the commercialization of aconitic acid production from "B" or second molasses. For several previous years work had been done only during the short grinding season on attempts to develop a suitable recovery process. At the close of the 1945-46 season a large supply of "B" molasses was obtained from a sugar mill and intensive laboratory and pilot plant research was carried out at the New Orleans Laboratory. The basis was established for a process yielding maximum recoveries without affecting the subsequent production of sugar. Pilot plant runs provided data on optimum conditions, design, and capacity of equipment, and operating methods whereby aconitate can be recovered continuously by diverting the molasses for little more than an hour and returning it to the mill without interruption of further sugar crystallizing operations.

Based on this research a plant of sufficient capacity to treat all of the "B" molasses of the largest mill in Louisiana, grinding 3,000 tons of cane per day, was installed at Raceland. It was operated throughout the grinding season and assistance was rendered by the staff of the New Orleans Laboratory in overcoming operating and mechanical difficulties, and in establishing suitable analytical and process control methods. Despite low mechanical efficiency of a new type of continuous centrifugal used to collect the product, over 140,000 lbs., or three carloads, of very high grade calcium-magnesium aconitate were produced and sold. Work is in progress on redesign of the centrifugal, and it is expected that this one mill will attain a production of between 400,000 and 500,000 lbs. of the product next season. There is evident demand for many times this amount of aconitic acid for use by manufacturers of plastics, especially for production of valuable plasticizers. Details of the process have been made available to the industry in Bureau Mimeograph Publication AIC-132, and other mills are interested in the possibility of adopting the process.

Sugarcane Wax

Work has continued at the Houma Laboratory on the extraction of sugarcane wax, and improved methods have been developed for refining the hard wax product. Attention has been given to the fatty fraction separated from the crude extract

and a number of higher alcohols, sterols, fatty acids and other constituents of possible value have been isolated. Complete identification of these substances is in progress. An authoritative treatise on the subject has been prepared for publication by the Sugar Research Foundation. Extraction of wax from clarification muds on a commercial scale is expanding in Cuba, and interest in the process is developing in the domestic industry.

Cane Juice Clarification

Attention has been given to the increasingly important problem of clarification of juice from mechanically harvested and burned cane, as well as from the new varieties being introduced. The effect of starch, and fat and wax impurities were investigated, and bentonite clarification at the normal pH was found to remove more wax than liming. Burned cane, especially during wet weather, yielded juice which could not be clarified with lime as the muds failed to settle at a practical rate. It was found in laboratory tests at New Orleans that a combination of lime and fuller's earth effected clarification of a soured juice, and in practice one of the mills was enabled to continue satisfactory operation during a period when especially bad juice from wet, burned cane was being processed. Fundamental research is planned to determine the nature of the substances causing abnormally slow settling, and the specific action of clarifying agents other than lime.

Sugar Beet Storage

Research on sugar beets conducted during the season in the Western beet area was upon reduction of sugar losses in beet storage piles. Based on results obtained in cooperation with Bureau of Plant Industry, Soils, and Agricultural Engineering on small samples placed in the piles, several large scale tests up to 40,000 tons in the largest pile, were carried out, using both surface whitewashing and forced night air circulation. Temperatures were thus reduced, and data will be obtained on costs of these methods and the saving of sugar effected.

Chemical and Microbiological Evaluation of Beet Sugar

Composite samples were received at New Orleans from all of the beet factories, and chemical and bacteriological evaluation of sugar quality factors were determined and reported as in past seasons.

FARM-MADE SIRUPS (SUGARCANE, SORGO, MAPLE AND MAPLE SUGAR) INVESTIGATIONS

Sorgo Sirup

Work on improvement of the quality of sorgo sirup by

filtration was continued at the Auburn Station, and investigation of the structure and properties of sorgo juice starch was initiated.

Candy Studies

A major investigation under this project is the development in cooperation with the National Confectioners' Association of established and new types of candies using a wider variety of agricultural products. Efforts are directed toward the incorporation of refined soy, peanut, and other proteins to improve the nutritional balance of the candies. New type centers using less sugar and including protein were developed by use of modified pectin with low methoxyl content. Fruit purees prepared at the Western Regional Research Laboratory have been used in various types, and assistance was given the Eastern Regional Research Laboratory in development of apple candies using apple essence and concentrate.

TUNG NUTS INVESTIGATIONS

Drying, Milling and Oil Extraction of Dehulled Nuts

The Laboratories at Gainesville and Bogalusa are in close contact with all American tung oil processors, and render assistance on practical problems in addition to conducting research on methods of extraction and improvement of oil quality. Attention has been given to the technical and economic factors involved in applying solvent extraction for recovery of tung oil from the meal. During the past year much of the work has been devoted to careful studies of drying of dehulled nuts and milling quality of such nuts after storage. Introduction of field hullers will require the mills to handle hulled rather than whole nuts, and conditions of drying were developed which permit the material to be stored for reasonable lengths of time without loss of efficiency in processing with the oil expellers generally in use.

LABORATORY OF FRUIT AND VEGETABLE CHEMISTRY
LOS ANGELES, CALIFORNIA
E. A. Beavens, In Charge

CITRUS

Standardization of Desert Grapefruit Juice

The sugar-acid ratio of Desert grapefruit varies over a wide range during the canning season, which makes it impossible for the canners to put up a uniform pack. If the excess acidity could be neutralized to a selected point by the addition of a cheap salt, and the solids content raised to a fixed Brix reading by the addition of sugar, then a standardized pack could be prepared throughout the entire season.

It has been demonstrated that small additions of basic salts to neutralize some of the high acidity of the early season grapefruit juice along with the addition of some sugar markedly improves the acceptability of the canned juice. As a result of this work, two commercial processors are planning to put up experimental packs of approximately 1000 cases, each to determine consumer acceptance and compliance with Federal Food and Drug laws.

Freezing Preservation of Citrus Purees

It appears from preliminary experiments that orange puree made from whole fruit and sweetened with sugar in the proportion of 4 to 1 and 5 to 1 can be frozen and stored at 0° F. for at least six months without developing a strong "terpeny" flavor which would prevent its use in the manufacture of a commercial orange ice. One of the local fruit freezing companies packed small quantities of this puree to do some cooperative work with a local ice cream company on the preparation of some orange ice samples. If this can be done without development of the "terpeny" flavor, it will mean large quantities of this type product can be processed and shipped East for use by the large ice cream companies.

Keeping Qualities of Chilled Fresh Citrus Juice

Chilled orange juice now being prepared for rapid distribution in Southern California has a storage life of only 3 to 4 days when kept at ordinary refrigerator temperatures. Investigation has shown that this juice is not deaerated, which undoubtedly accounts for its poor keeping qualities. Preliminary experiments on the processing of fresh orange juice have shown that the storage life of this product can be increased to 10 or 12 days if the juice is deaerated, stored in an air tight container and kept at 38° F. If this can be done under commercial conditions, the packers of fresh juice will be able to distribute a much better product than they now have.

Freezing Preservation of Citrus Segments

This past summer, a cutting of frozen grapefruit segments was held at the laboratory which was attended by approximately 30 people representing the citrus industry in Southern California and Arizona. The

segments had been packed under varying conditions of sugar concentrations and combinations of sugar, with and without deaeration, and the addition of ascorbic acid. The samples had been frozen at -25° F. and stored at -5° F. for six months.

The general conclusion of all present was that the best samples were those in which the covering liquid was either the natural grapefruit juice or natural grapefruit juice sweetened to 20° or 30° Brix by the addition of sugar. No improvement in flavor could be noted in the deaerated samples or those containing the added ascorbic acid.

A new series of samples are now being prepared each month during the present grapefruit season, using the juice syrups at the covering medium.

Quick Freezing of Citrus Juices

Considerable research work is needed at the present time to improve the quality of frozen citrus juices. Most companies ream the fruit, package the screened juice in cellophane bags, freeze in calcium chloride brine with the juice exposed to the air, seal and place the bags in cardboard containers. No effort is made to deaerate or pasteurize the juices and the freezing time takes from 45 to 60 minutes. Experiments are under way to study the effects of faster freezing using a rapid heat exchanger or slush freezer, filling the partially frozen juice into cans, hermetically sealing and finishing at -25° F. The effects of deaeration, pasteurization slow freezing versus rapid freezing, and packaging are being studied to determine their effects on the quality of the juices. Physical and chemical changes taking place in the stored juices are also being studied.

CANNED TOMATO PASTE

Chemical Composition of Commercial Tomato Paste

Work has been started on a project to determine the chemical composition of commercially canned tomato paste samples, and the influence of processing methods and types of equipment on the loss or alteration of constituents which may affect their quality, flavor, loss of vitamins and color. During the past tomato season, a survey was made through twelve commercial tomato paste processing plants in Southern and Central California to study the processing methods and types of equipment used and to obtain samples from each one for chemical analysis.

The effect of processing on the color reflectance and the carotene and lycopene content of the canned tomato paste samples is of particular importance. Color reflectance of the sixteen samples will be determined in the Hardy instrument at the Western Regional Research Laboratory. A new rapid procedure has been worked out for separating lycopene from the tomato paste in clear crystalline form. Chromatographic analysis of these crystals revealed little, if any, carotene or xanthophyll as contaminants. Colorless fatty substances decreasing adsorption were absent. A simple chromatographic method has been found for the separation of lycopene and carotene from tomato paste. Determination of the separated pigments may be made either with a colorimeter or spectrophotometer. Attempts to determine lycopene and carotene as constituents in a mixture have been unsuccessful.

FRUIT AND VEGETABLE PRODUCTS LABORATORY

PULLMAN, WASHINGTON

A. M. Neubort, In Charge

FRUIT PRODUCTS

Freestone Peach Canning Investigations

Studies on the effect of harvest maturity and method of ripening on the canning quality of the Elberta and J. H. Hale varieties of freestone peaches were repeated. These studies were first conducted in the 1945 season in cooperation with the Irrigation Branch Experiment Station at Prosser, and the Fruit and Vegetable Processing Laboratory of the Department of Horticulture in Pullman. For the harvest maturity study, fruit at eight stages of maturity, representing a range from early shipping-ripe to soft-ripe, were harvested for each variety. Descriptive data on maturity and data on chemical composition were obtained for each lot at the time of harvest. After ripening, all samples were again analyzed and representative lots were canned. For the ripening study, uniform lots of the Elberta and J. H. Hale varieties were ripened under varying conditions of temperature and humidity. Descriptive data were obtained on the maturity of each variety at harvest and chemical analyses were made. Similar data were again obtained on the fruit at progressive stages during ripening and representative samples were canned. Results of these studies will not be available until quality evaluation and chemical analyses of the canned samples have been completed. It is expected that these investigations will be completed when the results from the two seasons of study have been combined.

Better control of the color of commercially canned freestone peaches will be possible as a result of information obtained on the influence of processing methods on the color of this product. Studies in progress on the chemistry of peach pigments should lay the foundation for solving the problem of discoloration in the canned fruit of certain commercially available freestone peach varieties.

Canning Investigations on Apricots

Apricot production in Central Washington is expanding rapidly as a result of plantings on new land being brought under cultivation. Information being obtained on the canning quality of the different apricot varieties grown in this area will be very useful in determining suitable varieties for the new plantings. Preliminary results of studies in progress on methods of harvesting and ripening the Wenatchee Moorpark variety of apricots indicate that this variety may be adapted to processing uses if suitable handling procedures are employed. The Wenatchee Moorpark, now the most extensively grown variety in this area, is at present considered unsuitable for canning.

Detartration Studies on Grape Juice

Studies on the use of ion exchange treatment for controlling the acidity of grape juice promise to solve the acidity control problem of

the Pacific Northwest packers. By use of this process the packer could accurately control the acid content of juice and could achieve a more complete detartration. The process would also permit substitution of large tank refrigerated juice storage in place of the present storage in 5-gallon carboys.

Prefreezing Treatments of Freestone Peaches

These studies were continued in conjunction with the studies listed under Freestone Peach Canning Investigations. Representative samples from each lot of fruit were preserved by freezing. Results of these studies will not be available until quality evaluation can be completed and the data from the two seasons, 1945 and 1946, combined.

Information on the effect of harvest maturity and method of ripening on the quality of frozen peaches is needed by the rapidly growing freestone peach freezing industry. At present, serious losses in yield and quality are experienced by freezers because information regarding the effects of prefreezing treatment on quality is not well established.

VEGETABLE PRODUCTS

Froth Flotation Process

As a result of last season's commercial operation in three canneries in the Walla Walla area, the canning industry generally is being forced by the growers to accept the froth flotation process. Rejection of nightshade infested peas by canners not equipped with the process resulted in dissatisfaction among growers. The apparent marketability of peas containing possible traces of oil residue also is encouraging general acceptance of this process.

Canning Technology of Pacific Northwest Vegetables

Investigations on the canning technology of vegetables grown in the Lewiston, Idaho area were continued in cooperation with the Department of Horticulture, University of Idaho. Crops under study during the period included peas, sweet corn, tomatoes, and green beans. Canned pea samples prepared in the previous period were graded according to U. S. Grades. Results of these studies will not be available until data on yields and harvest periods can be summarized.

Results of studies on the canning technology of vegetables are proving of importance to the canning industry of this area. Three commercial pea canners are interested in the possibilities of establishing a green pea canning industry in the Palouse area. This area annually grows about 400,000 acres of dried peas. One commercial canner conducted private experimental plots during the past season. Further studies, including a series of planting dates, will be required before the suitability of the area for green peas can be determined. Tentative results on the tomato studies show John Baer, now one of the commercial varieties canned in the Lewiston area, to be less suitable than a number of others on the basis of wholeness and color.

Freezing Technology of Pacific Northwest Vegetables

Freezing studies were conducted on peas, sweet corn, green beans, and lima beans in conjunction with the studies on canning technology. Preliminary examinations were made on these samples but results will not be available until the data can be combined with results obtained by the Western Regional Research Laboratory in evaluating these samples.

Information being obtained by the study on freezing of vegetables will be useful to the rapidly expanding frozen food industries of the Pacific Northwest. At present many of the locations selected for growing crops and the varieties selected for freezing must be considered experiments on a commercial scale because technical data is not available.

ENZYME RESEARCH LABORATORY
Arnold Kent Balls, Head Chemist

The projects of the Enzyme Research Laboratory are considered to be essentially agricultural research. In the processing, shipment or storage of agricultural commodities, it is becoming more and more evident that a detailed knowledge of the agricultural processes of ripening (and when possible, some control of that process) would be of great advantage. Several projects in the Enzyme Laboratory have been directed toward the objective.

Stimulation of Ripening by Ethylene: It has been found that the ripening of grains, namely wheat and rice, is accelerated by ethylene after they are harvested. Such artificial ripening should result in decreasing the intensity of the "sweating" period which immature grain undergoes. An experiment on wheat indicated that this was the case. Further experiments, also on rice, are considered necessary.

The repeated treatment of harvested Navel oranges with ethylene resulted in a marked improvement in the flavor of the juice and a decrease in the bitter taste that develops on standing. This improvement was not enough to remove the bitter principle entirely and therefore experiments are underway to stimulate the ripening while the fruit is still on the tree. The oranges of these tests are not yet available so the results are still unknown.

Enzymes Connected with the Metabolism of Citrus and the Quality of Fruit: An enzyme capable of splitting phosphoric acid from certain organic phosphates has been found in the peel and juice of citrus fruits. Such reactions of phosphorous are probably involved in the carbohydrate metabolism of the fruit. The preparations of this enzyme (which may be mixtures), have also the property of transferring phosphoric acid from an organic phosphate to any one of a large number of alcohols. This is an unusual reaction that surely takes part in the formation of sugars or acids.

Oxygen transfer in citrus metabolism can take place (in part) through the decomposition of terpene peroxides by peroxidase. It was found that phenols and vitamin C may be oxidized in this way. The details and significance of the observation are being worked out in a collaborative study with the Los Angeles Laboratory.

Changes in Starch Digesting Enzymes (Amylases) Caused by Ripening: These changes have been followed in detail in wheat. The dextrin-forming amylase (alpha-amylase) appears to remain constant in quantity throughout the development and ripening of grain. This is the enzyme that increases so greatly on sprouting. On the other hand, the sugar-forming amylase (beta-amylase) increases as the grain grows in size and then apparently decreases as the grain ripens. The decrease is apparent only, for during the ripening the enzyme is changed from a soluble protein which is the active enzyme to an insoluble and also inactive protein. When the inactive protein is partially broken down by a proteolytic enzyme, it is again changed to soluble and active amylase. Therefore,

the total amount of amylase present in wheat remains constant during ripening, but its apparent activity decreases. Since proteolytic enzymes are active during sprouting, the reappearance of active amylase at that time is readily understandable.

The preparation of malt is essentially a sprouting process and the best malt is known to be that which shows a definite proportion between the dextrin-forming and the sugar-forming enzymes. Sometimes the increase in dextrin-forming enzyme is greater than the re-activation of sugar-forming enzyme should be. Then the malt is poor because it is low in sugar-forming enzyme. We found that such malt may be improved by adding extra sugar-forming enzyme from another source. One of the richest sources is the sweet potato. The enzyme (beta-amylase) occurs in the juice of sweet potatoes, and may be separated from the starch simply by pressing.

Since the press juice from sweet potatoes was found to be so very high in beta-amylase, experiments were made to concentrate and purify the enzyme from that source. The results led to the preparation of crystalline beta-amylase which has thus become the first enzyme of carbohydrate hydrolysis to be obtained in the pure state.

Ripening and Changes in Fat: The appearance of fat during the development of olives has been followed throughout the present year, in the hope of finding a fat-splitting enzyme during some stage of the growth or ripening. Data showing correlation between fat content, age and size have been obtained, but no lipase was found during the entire course of this work. Either our technique omits some essential detail or else the fat-splitting and rancidity that so frequently develop in impure oils is due to other causes. Similar work on ripe rice during storage has also given negative results for lipase, although rice oil develops rancidity and free fatty acids with extreme ease. One observation that may turn out to be a valuable lead has been made. It was found that fat-splitting and rancidity in rice could be accelerated by subjecting the grain to high pressure for a short time.

Phytochemical Studies: The importance of lipoproteins in lipid metabolism is rapidly being recognized. We have prepared the protein part of one such complex from wheat flour. The preparation was subsequently purified and obtained in crystalline form. It has been named "purothionin" because of its source (wheat), and the fact that it has the highest sulfur content as yet observed for any pure protein. It is essentially a protamine and is quite toxic to many microorganisms and (on injection) to small animals. If this protein were re-combined with a lipid, its function should be easier to discover. The need for a lipid of known and definite composition to combine with the protein led us to attempt the synthesis of cephalin. We have succeeded in synthesizing dipalmitocephalin in good yields by what is thought to be an entirely new reaction for such a property (condensation of ethanolaminephthalimide with dipalmitoglycerophosphoric acid and subsequent removal of phthalic acid with hydrazine). Great care was taken to establish the constitution of this synthetic cephalin beyond a doubt because its properties do not check with those in the literature by the other worker who reported having made this substance. A patent on our synthesis has been asked for.

George W. Irving, Jr., Head

BASIC INVESTIGATIONS IN THE CHEMISTRY OF AGRICULTURAL PRODUCTS

Investigations on the Biochemistry of Plant Disease Resistance

Experimentation has been continued in the investigation of economically important plants for the presence of chemical substances (antibiotic agents) that may be responsible for the resistance that certain varieties of these plants offer to disease causing microorganisms.

A substance designated "tomatin", which inhibits the growth of the fungus (*Fusarium*) that causes wilt disease in tomatoes, has been found to be present in the tomato plant. Experiments indicate that tomatin probably plays an important role in the defense mechanism of the tomato toward the wilt-causing fungus. Antibiotic agents possessing tomatin-like activity have also been found to occur in several other economically important plants and it is believed that these tomatin-like substances may be responsible, at least in part, for the disease resistance of these plants. This work partially substantiates a new concept regarding the mechanism of disease resistance in plants. Because of the seriousness of plant disease as an agricultural problem, full and immediate exploration of this new, promising concept is being undertaken.

In addition to its pronounced effect upon plant disease organisms, tomatin has also been found to exert strong inhibiting action toward the growth, in culture, of many of the fungi that cause disease in man and animals. This is highly significant since the medical profession has no drug which is effective in controlling fungus infections even though they are among the most prevalent and serious of human diseases. Co-operative experiments with the Duke University Medical School, Durham, N. C. have shown that the tomatin preparations now available are sufficiently non-toxic to permit limited parenteral administration in experimental animals and efforts are being made to accelerate the in vivo testing of tomatin to ascertain its possible therapeutic value.

Investigations on the Mechanism of Action of Plant Growth Regulating Substances

Research has continued on the synthesis of chemical compounds (plant hormones) that are capable of modifying the growth process in plants and on the investigation of the mode of entry, transport and mechanism of action and fate of these compounds in the plant.

The application of organic chemicals to plants to produce modifications in the rate and type of growth is now widely practiced experimentally. Since these effects are produced by the application to the plant of infinitesimal amounts of different chemical compounds, the cost of such treatment is small enough to permit farm-scale application with resulting increases in both the quantity and quality of agricultural crops. However, in some cases hormones produce, simultaneously, undesirable as well as desirable

effects on the plant. If plant hormones are to be used efficiently, the hormones that produce the maximum of desirable and the minimum of undesirable effects must be found. To accomplish this, the mechanism of action in the plant of a given plant hormone must be thoroughly investigated and understood so that a fundamental basis for evaluating hormonal activity in terms of chemical structure can be established.

It has been possible for this Division to take immediate advantage of new research tools recently made available for biochemical research of this type, namely, the radioactive chemical elements resulting from atomic bomb investigations carried out during the War. A plant growth regulator, containing radioactive iodine as a tracer atom, was synthesized, applied to bean and barley seedlings and its entry and translocation in the test plants was followed by measurement of the radioactivity of various parts of the plant. By this means it was possible to demonstrate for the first time that a plant growth regulator is absorbed by both bean (dicot.) and barley (monocot.) plants, that it is translocated predominantly to the terminal bud and hypocotyl of the bean plant where greatest reduction in growth occurs, and that it is translocated predominantly to the second leaf of barley plants where growth inhibition is insignificant. Since the growth regulator is absorbed by both bean and barley plants it must be inferred that the growth inhibiting effects of the regulator in dicotyledonous plants and the failure of the regulator to produce significant inhibition in monocotyledonous plants must be due either to differences in the regulator concentrations in the two plant types or to difference in the manner in which the regulator reacts with the plant constituents in each case. Experiments are continuing to ascertain which of these two alternatives is correct and to gain information on the nature of the plant constituents with which the growth regulator combines to exert its effect on the metabolic process of the plant.

PHARMACOLOGY INVESTIGATIONS

Citrinin.

Citrinin is an antibiotic produced by *Penicillium citrinum* when grown on a culture medium derived from waste asparagus butts. Investigations on the toxicity, pharmacological properties, and mechanism of action of citrinin have been completed and the results published in *The Journal of Pharmacology and Experimental Therapeutics*. Citrinin was found to have pharmacological actions similar to those of pilocarpine and acetylcholine.

Nicotine Derivatives.

The acute toxicities of l-nicotine and myosmine were determined, and the actions of the two compounds on the isolated intestine, and uteri of guinea pigs were studied. Myosmine was found to have about one-tenth the acute toxicity of l-nicotine after oral administration and one-sixth after intraperitoneal administration. Myosmine in a concentration of 1:12,500 caused contractions of intestinal segments similar to those produced by l-nicotine in a concentration of 1:2,500,000. Neither compound had any effect on the isolated uterus.

Rutin.

Rutin, a rhamno-glucoside of quercetin, obtained from buckwheat has been shown to be beneficial in clinical cases characterized by abnormal permeability or fragility of the capillaries. To obtain an understanding of the mechanism of action of rutin its pharmacological properties are being investigated. Rutin has been shown to inhibit the oxidation of epinephrine and to prolong its action on smooth muscle structures. Under appropriate conditions of dosage and time of administration rutin has been shown to prevent death from histamine in guinea pigs.

Ascorbyl Palmitate.

Ascorbyl palmitate is a fat soluble derivative of ascorbic acid prepared by the Eastern Regional Laboratory and shown to have antioxidant properties. Pharmacological studies have shown that the low serum phosphatase values characteristic of scorbutic guinea pigs are raised to comparable levels by equimolecular amount of ascorbic acid and ascorbyl palmitate. Ascorbyl palmitate is therefore a fat soluble source of vitamin C.

Cottonseed Meal.

The Southern Regional Laboratory has developed a process for defatting cottonseed meal and removing the pigment glands. Toxicity studies on the defatted-depigmented meal have shown that rats eating a diet containing as high as 30 per cent of the meal grew as well as control rats, but that rats eating a diet containing as little as 0.25 per cent of the pigment gland fraction showed a significant inhibition of growth. This investigation proved that the toxic factor in raw cottonseed meal is in the pigment gland fraction.

Continuous Saccharification Process.

Toxicity tests have been made on the by-product feed material resulting from the continuous saccharification process developed at the Northern Regional Laboratory. When 15 per cent or more of this product was incorporated in the basic diet of experimental rats inhibition of growth occurred. The product contains appreciable quantities of calcium and sodium sulfate, and it has been shown that feeding comparable concentrations of these two salts produced a similar inhibition of growth.

Starch Powders.

Various starch powders have been prepared by the Northern Regional Laboratory. It was hoped that one use for these starches would be as a substitute for talc in powdering surgeon's rubber gloves. The five starches tested were found to vary in their powdering characteristics, ability to withstand autoclaving, and in their freedom from causing foreign body reactions in the peritoneal cavities of experimental animals.

Vernon H. McFarlane, Acting Head of Division

MICROBIOLOGY OF DRIED EGGS AND RELATED EGG PRODUCTS *

Occurrence of Multiple Salmonella Types in Spray-Dried Whole Egg Powder

From 2 to 30 presumptive Salmonella-positive colony isolates were identified serologically in each of 171 samples of high (4 to 6%) moisture spray-dried whole egg powder (manufactured for Lend-Lease shipment). Findings demonstrated that egg powder is frequently contaminated with more than one Salmonella type. For example, as many as six types were isolated from each of two egg powder samples from which 20 to 30 colony picks were made. Although combinations of types differed, no one combination was more common than another. In general, the probability of isolating more than one Salmonella type per sample is increased as the number of presumptive-positive colony isolates identified per sample is increased.

Paracolon Organisms in Spray-Dried Whole Egg Powder

Of 164 paracolon cultures isolated from as many samples of egg powder, 117 which were forwarded to Dr. P. R. Edwards (Lexington, Kentucky, Salmonella Typing Center) were found to be antigenically related to the "Arizona" group. Fourteen of the 19 antigenic combinations within the Arizona group were represented. The 117 cultures were lactose +, sucrose -, H₂S + and indol -. They failed to give reactions with the five basic Salmonella "O" sera (B, C₁, C₂, D, E).

Incidence of Salmonella Types in and on Shell Eggs

Salmonella organisms were isolated from 30 out of 2,577 meats and from 13 out of 2,129 shell scrapings. The 30 isolations made from the meats all belonged to Group D (Kauffmann-White Schema) and were identified as S. pullorum. The 13 isolations made from the shell scrapings fell into Groups C₁ and E and were identified as S. montevideo and S. anatum.

* These investigations were undertaken in cooperation with the Poultry Branch, Production and Marketing Administration, U. S. Department of Agriculture, Washington, D. C. and/or the Quartermaster Food and Container Institute for the Armed Forces, Chicago, Illinois.

Effect of Holding and Scrambling on *Salmonella* in Reconstituted Egg Powder

Salmonella were found to multiply rapidly in reconstituted egg powder held at temperatures ranging from 25° to 45° C. Findings confirmed the observation of Haines and Elliot (J. Hyg. 43:370, 1944) that "the period of rehydration should not exceed four hours." While holding reconstituted egg is not advised, it is evident that any holding should be at refrigeration temperatures. *Salmonella* were recovered from test scrambles (soft) prepared from both artificially and naturally contaminated reconstituted egg powders.

The work of the Naval Stores Research Division is divided: roughly, two thirds of it is done in New Orleans, and the other third at the Naval Stores Station, Olustee, Florida. The chief lines of investigation at present are outlined below.

INVESTIGATION OF NAVAL STORES PRODUCTION,
PROCESSES AND EQUIPMENT

Processing of Pine Gum

During the past two years, a new and improved method has been developed for the continuous flash distillation of pine gum. Heretofore, all pine gum has been distilled in small batch stills. The new method provides for continuous distillation at atmospheric pressure. This results in a more uniform product, better steam economy, and a marked reduction in labor costs. A small commercial size continuous flash still has been designed, built, and operated. A public demonstration of this still, held early in December 1946, created a great deal of interest and much favorable comment throughout the industry. These studies will be continued on a larger scale in cooperation with various naval stores producers.

Studies of Cup and Gutter Materials

Gum rosin producers are showing increasing interest in the use of sulfuric acid to stimulate the flow of gum from pine trees, as advocated by the Forest Service. This necessitates a search for cup and gutter materials which will be acid-resistant. Tests have been conducted at the Naval Stores Station with aluminum, stainless steel, and vitreous enamelled steel. To date, no entirely satisfactory material has been found. These tests are being continued, together with various synthetic resin coatings.

INVESTIGATION OF THE COMPOSITION, COMPONENTS
AND DERIVATIVES OF NAVAL STORES

Synthetic Elastomers from Turpentine Derivatives

Products, such as isoprene and myrcene derived from the alpha and beta pinene, respectively, of gum turpentine, have been copolymerized with styrene under a wide variety of conditions. Some of the isoprene-containing polymers show a relatively high tensile strength and elongation when compounded and vulcanized according to standard techniques.

Chemical Derivatives of the Pinenes

Work has been continued on the development of useful chemical derivatives of alpha and beta pinene. These include hydration products, chlorinated compounds, and others. Basic information on the reactions and structures of these compounds is being accumulated with the ultimate object of developing new industrial uses for turpentine.

INVESTIGATION OF THE USES OF NAVAL STORES

Purification of Dehydrogenated Rosin

Increasingly large quantities of catalytically dehydrogenated rosin are being used in the manufacture of synthetic rubber, specifically GR-S 10. Certain impurities are present in the product which decrease the rate of polymerization and/or the yield of polymer. It has been found that if the dehydrogenated rosin be dissolved in petroleum naphtha and percolated through towers of fullers earth or other adsorbent silicates, the undesirable impurities are removed and an improved dehydrogenated rosin is obtained. This gives better yields of polymer when used as an emulsifier. The impurities adsorbed on the fullers earth are easily dissolved off with alcohol so that the adsorbent can be used over and over again. After a patent application had been filed, this method of purification was discussed with a commercial producer of dehydrogenated rosin.

Utilization of Resin Acids

Considerable work has been done on the preparation of the maleic anhydride adduct of l-pimaric acid from pine gum. The conditions necessary for the nearly quantitative separation of this adduct have been determined. It has also been found that varnishes having excellent hardness and water resistance can be prepared by esterifying the mixed mono- and diglycerides of linseed oil with this addition product of maleic anhydride and l-pimaric acid. Further studies are under way on the effect of acid stimulation of pine trees on the composition of the pine gum produced and the effect of such changes, if any, on the utilization of the rosin obtained.

Compilation of Statistics

Comprehensive statistics have been compiled and published quarterly on the production, consumption, and stocks of rosin, turpentine, and other naval stores products. Such data are of considerable value to both producers and consumers of naval stores products.